The selection and application of analytical methods for the measurement of trace amounts of dicarboxylic acids in the air

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CONTENTS

LIST OF ABBREVIATIONS AND ACRONYMS

BC/EC	Black carbon or elemental carbon
C=O	Carbonyl functional group
C_2	Oxalic acid (etanedioic acid)
C_3	Malonic acid (propanedioid acid)
C_4	Succinic acid (butanedioic acid)
C_5	Glutaric acid (pentanedioic acid)
C_6	Adipic acid (hexanedioic acid)
C_7	Pimelic acid (heptanediodic acid)
C_8	Suberic acid (octanedioic acid)
C_9	Azelaic acid (nonanedioic acid)
C_{10}	Sebacic acid (decanedioic acid)
C_{11}	Undecanedioic acid
C_{12}	Dodecanedioic acid
CCN	Cloud condensation nuclei
COH/OH	Alcohol functional group
COOH	Carboxylic acid
Diacids	Dicarboxylic acids
DOC	Dissolved organic carbon
F	Fumaric acid
GC-FID	Gas chromatography-flame ionization detector
GC-MS	Gas chromatography-mass spectrometer
H^1-NMR	Proton nuclear magnetic resonance
hC_4	Malic acid
HPLC	High-performance liquid chromatography
HRGC-MS	High resolution gas chromatography-mass spectrometer
IC	Ion chromatography
ICS-3000 RFIC	Reagent free ion chromatography
IEC	Ion exchange chromatography
IN	Ice nuclei
LMW	Low molecular weight
M	Maleic acid
mM	Methylmaleic
MWSOC	Macromolecular fraction of WSOC

NH_4^+	Ammonia
NMHC's	Non methane hydrocarbons
NMR	Nuclear magnetic resonance
NO_3^-	Nitrous compound
OC	Organic carbon/compounds
Ph	Phthalic acid
PM	Particulate matter
SEC	Size exclusion chromatography
SO_4^{2-}	Sulphurous compound
SOA	Secondary organic aerosols
TC	Total carbon
TOC	Total organic carbon
TSP	Total suspended particles
UF	Ultra filtration
VOC's	Volatile organic compounds
WSOC	Water soluble organic carbon/compounds

ABSTRACT

Carbonaceous aerosol components which consist of organic compounds (OC) and black carbon (BC) account for a large fraction of atmospheric particulate matter. Most information available on the abundance, properties, and effects of these components so far is based on measurement data of total carbon (TC = OC + BC). This data is increasingly complemented by measurements of water soluble organic carbon (WSOC), its macromolecular fraction (MWSOC), and individual organic compounds due to its environmental significance.

WSOC are usually highly polar, oxygenated compounds containing two or more COOH, C=O and/or OH functional groups such as hydroxyamines, amino acids, polyalcohols, sugars, dicarboxylic acids, ketocarboxylic acids and dicarbonyls. These compounds contribute to the ability of particles to act as cloud condensation nuclei (CCN) and dicarboxylic acids especially can potentially affect the global climate by scattering incoming solar radiation, which counteracts the global warming caused by the increase of greenhouse gases. According to literature the burning of cellulose (biomass burning) generates smoke particles that were nearly 100% water-soluble.

The Vaal Triangle was recently declared as the first priority area in South Africa by the Minister of Environmental Affairs and Tourism on the 21st of April 2006. The area comprises of heavy industrial activities, one power station, several commercial operations, motor vehicles as well as many households utilizing coal as an energy source. Ambient aerosol sampling for this study was done at 3 sites in the Vaal Triangle (Vereeniging, Vanderbijlpark and Sasolburg) during the winter of 2006 and summer of 2007 with Mini-volume portable air samplers. Aerosol samples were collected on pre-fired quartz filters.

Gas and Ion chromatography were applied in analyzing the aerosol filters for specific dicarboxylic acids in the WSOC fraction. However, the GC-MS method required the water extracted samples to be derivatized before injection. This multiple synthesis pathway proved difficult and errors prone with potential dicarboxylic acid loss since the dicarboxylic acids are present in ng/m^3. This meant the GC-MS was only used as a quantitative technique.

An alternative ion chromatographic method of analyzing dicarboxylic acids was developed. A new Dionex ICS-3000 RFIC instrument along with its special licensed software (Virtual Column) was utilized. The Virtual Column software makes it possible to simulate possible separations of predetermined individual compounds within the WSOC fraction. The influence and impact of various parameters can be checked without wasting valuable sample. After a method was developed, it was tested practically by analyzing standard solutions. The optimized method was then used to analyze the field samples collected at the different sites.

The ICS-3000 RFIC with Virtual Column proved to be a convenient and appropriate technique. It showed that the dicarboxylic acid species oxalic, malonic, succinic, glutaric and phthalic as well as inorganic ions fluoride, chloride, nitrate and sulphate were present in the air of all the sites. The chromatographic profile of all the sites also closely resembled each other, be they residential, industrial or petrochemical.

However, the methodology was only developed for qualitative analysis and further studies should develop the method further to include quantitative analysis as well.

OPSOMMING

'n Belangrike komponent waaruit aerosols in die atmosfeer bestaan is die koolstoffraksie wat saamgestel word deur die koolstof in organiese verbindings en swart koolstof. Inligting aangaande hierdie fraksie se hoeveelheid, eienskappe en gevolglike effek is tot dusver bepaal deur data aangaande die totale koolstof inhoud (Totale koolstof = organiese koolstof + swart koolstof). Hedendaags word hierdie data toenemend aangevul deur inligting bekom uit die bestudering van die wateroplosbare organiese fraksie, die makromolekulêre fraksie van eersgenoemde en analisering van individuele organiese verbindings weens die verbindings se invloed op die omgewing.

Die wateroplosbare organiese fraksie is gewoonlik hoogs polêre suurstof draende verbindings met twee of meer COOH, C=O en/of OH funksionele groepe soos aangetref in hidroksieamiede, aminosure, poli-alkohole, suikers, dikarboksielsure, keto-karboksielsure en dikarboniele. Wateroplosbare organiese verbindings het die spesiale vermoë om as kerne te dien waar om kondensasie plaasvind tydens wolkvorming. Dikarboksielsure spesifiek het die potensiaal om die globale klimaat te verander deurdat hierdie verbindings straling, en dus aardverwarming teen werk. Studies het getoon dat die verbranding van sellulose materiaal, dus o.a. veldbrande, lei tot die vorming van verbindings wat feitlik 100% wateroplosbaar is.

Op 21 April 2006 is die Vaal Driehoek as eerste prioriteitsgebied in Suid-Afrika veklaar deur die Minister van Omgewingsake en Toerisme. Faktore wat gelei het tot hierdie benoeming is o.a. grootskaalse nywerhede, 'n kragstasie, verskeie kommersiële instansies, emissies weens swaar verkeer sowel as grootskaalse steenkoolverbruik deur plaaslike nedersettings. Vir hierdie studie is 3 moniteringsareas binne die Vaal Driehoek (Vereeniging, Vanderbijlpark en Sasolburg) gekies vir die verkryging van lugmonsters gedurende die winter van 2006 en somer 2007. Mini-volume draagbare lugtoestelle is gebruik vir die opvang van lugmonsters op vooraf behandelde kwarts filters.

Gas- (GC) en ioon chromatogrfie (IC) was aangewend as analise tegnieke vir die opsporing van 'n seleksie van dikarboksielsure in die wateroplosbare organiese fraksie van die lugmonster filters. Die gas chromatografie metode het egter vereis

dat die water ekstraksie eers gederivatiseer moet word voor inspuiting in die GC in. Derivatisering in hierdie geval was 'n meerstappige sintese weg wat moeilik en potensieël tot dikarboksielsuur konsentrasie (ng/m^3) verlies gelei het. Weens hierdie rede was die GC-MS net aangewend as kwalitatiewe tegniek.

'n Alternatiewe ioon chromatografiese metode is ontwikkel vir die opsporing en analisering van die dikarboksielsure. 'n Nuwe Dionex ICS-3000 reagens vrye ioon chromatograaf met spesiale gelisensieerde sagteware, Virtual Column, is toe aangewend. Die Virtual Column sagteware maak dit moontlik om geselekteerde verbindings binne die wateroplosbare fraksie te simuleer. Sodoende word die impak en invloed van verskeie parameters bepaal sonder dat kosbare monster verbruik word. So is 'n teoretiese metode ontwikkel wat verder geoptimaliseer is deur die toepassing van die metode op standaard oplossings. Die finale metode was toe gebruik vir die analisering van die lugmonster van die onderskeie moniterings areas.

Die ICS-3000 reagens vrye ioon chromatograaf met sy sagteware Virtual Column was a gerieflike en toepaslike instrument vir die analisering van water oplosbare organiese verbindings. Die instrument het getoon dat oksaal, maloon, suksien, glutaar en phthaal dikarboksielsure sowel as die anorganiese ione fluoried, chloried, nitried en sulfied teenwoordig was by al die moniterings areas. Verder het die chromatografiese profiele van die onderskeie residensiële, industriële en petrochemiese moniterings areas baie nou ooreengestem.

Alhoewel die ICS-3000 reagens vrye ioon chromatograaf en die sagteware (Virtual Column) gunstige resultate getoon en geslaag het as analise tegniek, was die metodologie net ontwikkel vir kwalitatiewe analises. In verdere studies word daar aanbeveel dat die metode uitgebrei word om kwantitatiewe analises ook in te sluit.

CHAPTER 1
MOTIVATION AND GOALS

This chapter gives an introduction to the study. The motivation, as well as the objectives of the study is outlined.

1.1. BACKGROUND

Air pollution is generally thought of as a phenomenon characteristic only of large urban centers and industrialized regions, where concentrations may reach several orders of magnitude greater than ambient background levels. In the broadest sense, however, air pollution is a global problem, since pollutants ultimately become dispersed throughout the entire atmosphere (Seinfeld, 1986). Substantial evidence has accumulated that air pollution affects the health of human beings and animals, damages vegetation, soils and deteriorates materials, affects climate, reduces visibility and solar radiation, contributes to safety hazards, and generally interferes with the enjoyment of life and property (Seinfeld, 1986).

An aerosol is generally defined as a suspension of liquid or solid particles in a gas, with particle diameters in the range of 10^{-9}–10^{-4} m (lower limit: molecules and molecular clusters; upper limit: rapid sedimentation) (Seinfeld and Pandis, 1998). In atmospheric research the term "fine air particulate matter" is usually restricted to particles with aerodynamic diameters ≤1 μm (PM_1) or ≤2.5 μm ($PM_{2.5}$). In air pollution control it sometimes also includes larger particles up to 10 μm (PM_{10}) (Pöschl, 2005). In general, the dominant chemical components in atmospheric particulate matter (PM) are sulphate, nitrate, ammonium, sea salt, mineral dust, organic compounds, and black or elemental carbon (BC/EC), each of which typically contribute about 10–30% of the overall mass (Pöschl, 2005) as can be seen in Figure 1.

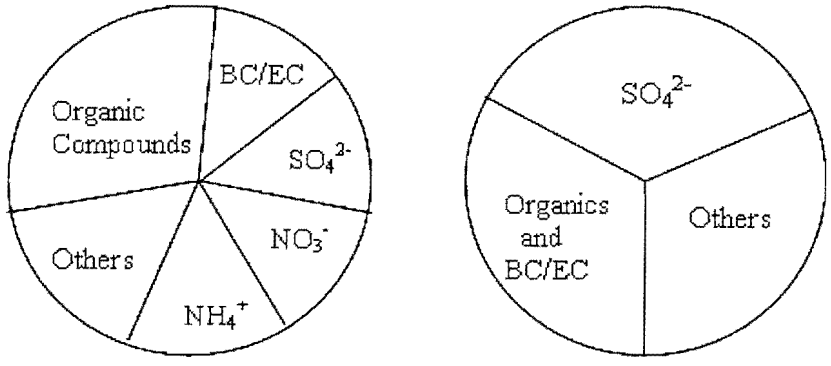


Figure 1: *Typical examples of aerosol chemical composition in urban (left) and higher alpine air (right) (Pöschl, 2005).*

Carbonaceous aerosol components (organic compounds and black (BC) or elemental carbon (EC)) account for a large fraction of air particulate matter (Pöschl 2005). Most information available on the abundance, properties, and effects of carbonaceous aerosol components is based on measured data of total carbon (TC), organic carbon (OC), and BC or EC (Kanakidou *et al.,* 2005). This data is now increasingly complemented by measurements of water-soluble organic carbon (WSOC), its macromolecular fraction (MWSOC), and individual organic compounds (Pöschl, 2005).

1.2. MOTIVATION

In South Africa, the need for stronger legislation and pollution monitoring has recently arisen. The Air Quality Act 39 of 2004 has made provision for the identification of priority areas where the air quality is regarded as poor and detrimental to human health and the environment. The Vaal Triangle (i.e. Sasolburg, Vereeniging and Vanderbijlpark) was declared the first priority area in South Africa by the Minister of Environmental Affairs and Tourism on the 21st of April 2006. The area comprises of heavy industrial activities, one power station, several commercial operations, motor vehicles as well as many households utilizing coal as an energy source (VTPA AQMP Baseline Report, 2007).

The study of the water soluble organic compounds (WSOC) in aerosols has recently become an active research area worldwide. Studies up until now were mostly

conducted in the northern hemisphere in Tokyo (Kawamura and Yasui, 2005), Hong Kong (Ho *et al.,* 2006), Los Angeles (Kawamura and Kaplan, 1987), and Italy (Decesari *et al.,* 2001). In the southern hemisphere studies have been conducted in Antarctica (Kawamura *et al.,* 1996) and New Zealand (Wang and Shooter, 2004). WSOC contribute to the ability of particles to act as cloud condensation nuclei (CCN) and are involved in the complex and almost unknown organic liquid phase chemistry of clouds (Decesari *et al.,* 2001). The burning of cellulose (biomass burning) also showed to generate smoke particles that are nearly 100% water-soluble (Graham *et al.,* 2002). Environmental measurements of the molecular form of WSOC are still lacking though.

This study was undertaken as a first study of this nature in South Africa to obtain ambient data of WSOC by selecting three monitoring sites in the Vaal Triangle. The goal was to analyze the filter samples collected from Sasolburg, Vereeniging and Vanderbijlpark for specific compounds within the WSOC fraction.

1.3. OBJECTIVES OF THE STUDY

The objectives of this study were:

1. Collect PM_{10} and $PM_{2.5}$ fractions at 3 selected monitoring sites in the Vaal Triangle using Airmetrics MiniVol Portable Air Samplers;

2. Develop an analytical method for identifying and quantifying individual compounds within the WSOC fraction in ambient air by using
   - Gas chromatography-Mass spectrometry (GC-MS) and
   - Ion Chromatography (IC) as analytical techniques for the identification of the individual WSOC;

3. Use the developed methods to analyze the filters obtained from the three monitoring sites.

CHAPTER 2
LITERATURE STUDY

This chapter discusses the literature information that is relevant to this study starting with aerosols, followed by water soluble organic compounds and dicarboxylic acids. Sinks and sources, possible formation mechanisms, seasonal and diurnal variations, as well as previous studies are discussed. Finally the different methods of analyzing water soluble organics are reviewed.

2.1. AEROSOLS

Aerosols are of central importance to atmospheric chemistry and physics, the biosphere, climate, and public health. The airborne solid and liquid particles in the nanometer to micrometer size range influence the energy balance of the earth, the hydrological cycle, atmospheric circulation, and the abundance of greenhouse and reactive trace gases. Moreover, they play important roles in the reproduction of biological organisms and can cause or enhance diseases. The primary parameters that determine the environmental and health effects of aerosol particles are their concentration, size, structure, and chemical composition. These parameters, however, are spatially (geographically) and temporally (time) highly variable. The quantification and identification of biological particles and carbonaceous components of fine particulate matter in the air represent demanding analytical challenges (Pöschl, 2005).

Motivated by global change and adverse health effects of traffic-related air pollution, aerosol research has been intensified increasingly over the past couple of decades (Pöschl, 2005). Aerosol effects on climate are generally classified as direct or indirect with respect to radiative forcing of the climate system. Radiative forcings are changes in the energy fluxes of solar radiation (maximum intensity in the spectral range of visible light) and terrestrial radiation (maximum intensity in the infrared spectral range) in the atmosphere, induced by anthropogenic or natural changes in atmospheric composition, earth surface properties, or solar activity. Negative

forcings such as the scattering and reflection of solar radiation by aerosols and clouds tend to cool the earth's surface, whereas positive forcings such as the absorption of terrestrial radiation by greenhouse gases and clouds tend to warm it (greenhouse effect) (Houghton *et al.,* 2001).

To better understand aerosols, the life cycle of a particle has to be kept in mind (Figure 2.1). Key elements to consider are firstly the source(s) of emission, life expectancy of the particles and thus how long the aerosol is airborne, the distance the aerosol travels, the distribution of the particles and lastly the sinks by which the aerosol is removed from the atmosphere. All these elements are important to determine where the aerosols came from and thus the chemical nature of the particles, how it is distributed in the atmosphere, if and how it will impact regional or locally on the environment and living organisms and lastly how the particles are removed from the atmosphere.

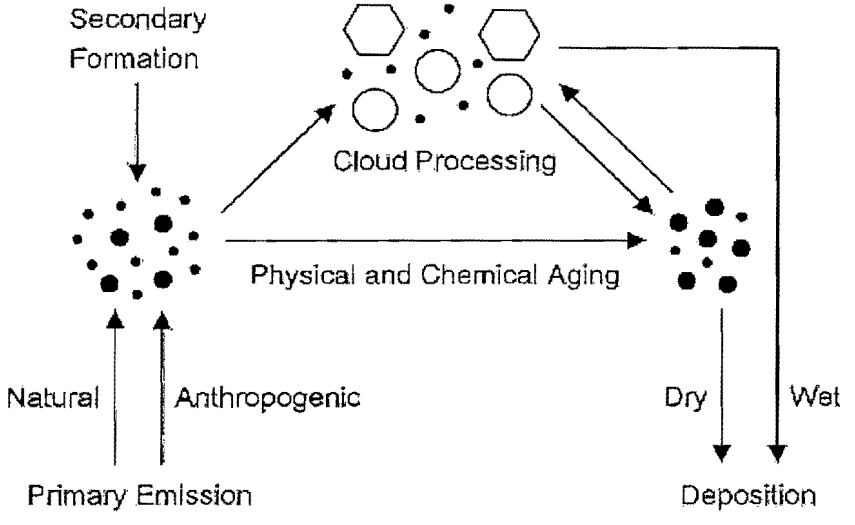


Figure 2.1: *Atmospheric cycling of aerosols (Pöschl, 2005).*

Atmospheric aerosol particles originate from a wide variety of natural and anthropogenic sources. Primary particles are directly emitted as liquids or solids from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, and wind-driven or traffic-related suspension of road, soil, and mineral dust, sea salt and biological materials (plant fragments, micro-organisms, pollen, etc.). Secondary particles, on the other hand, are formed by gas-to-particle

conversion in the atmosphere (new particle formation by nucleation and condensation of gaseous precursors) (Pöschl, 2005).

Depending on local sources, meteorological conditions, atmospheric transport, location, season and time of day, the composition of organic particulate matter (OPM) can be dominated by primary organic aerosol (POA) or by secondary organic aerosol (SOA) components (Pöschl, 2005). As mentioned in Chapter 1 the predominant chemical components of atmospheric particulate matter (PM) are sulphates, nitrates, ammonium, sea salts, mineral dust, organic compounds/carbon (OC) and black or elemental carbon (BC/EC). Most of these classes in turn can be subdivided into different groups making an aerosol a complex matrix to define.

2.1.1. Organic or carbonaceous compounds

Particulate matter (PM) in the lower atmosphere is composed of highly water soluble inorganic salts, insoluble mineral dust and carbonaceous material. This last fraction includes organic compounds ranging from very soluble to insoluble, as well as elemental carbon (EC/BC) (Jacobsen *et al.,* 2000). Fine particles are identified as a separate component of the total aerosol because they are usually chemically different from the coarse particles and have different sources, much longer atmospheric lifetimes and very different effects (Jacobsen *et al.,* 2000).

Unlike the salt and soil dust fractions, the organic compounds cover a wide range of molecular forms, solubilities, reactivities, and physical properties, which makes a complete characterization extremely difficult (Jacobsen *et al.,* 2000). Consequently, there is still no complete inventory of the chemical compounds that compose the fine-particle organic aerosol from any site in the world, and there is only limited understanding of the sources, sinks, transport, and transformation processes of these particles and their effects (Jacobsen *et al.,* 2000).

In terms of the composition of atmospheric aerosols, the organic fraction is a large contributor and is usually found in the fine particle mode (Cao *et al.,* 2005). The PM_{10} fraction though is also important with carbonaceous constituents such as elemental carbon (EC), as well as organic compounds contributing a large portion of

the overall mass of the coarse fraction (Sillanpää *et al.*, 2005). Organic compounds usually consist of 20-40% of particle mass from which typically only 45-60% is extractable and eluted on chromatographic columns (Rogge *et al.*, 1993) as is illustrated in Figure 2.2.

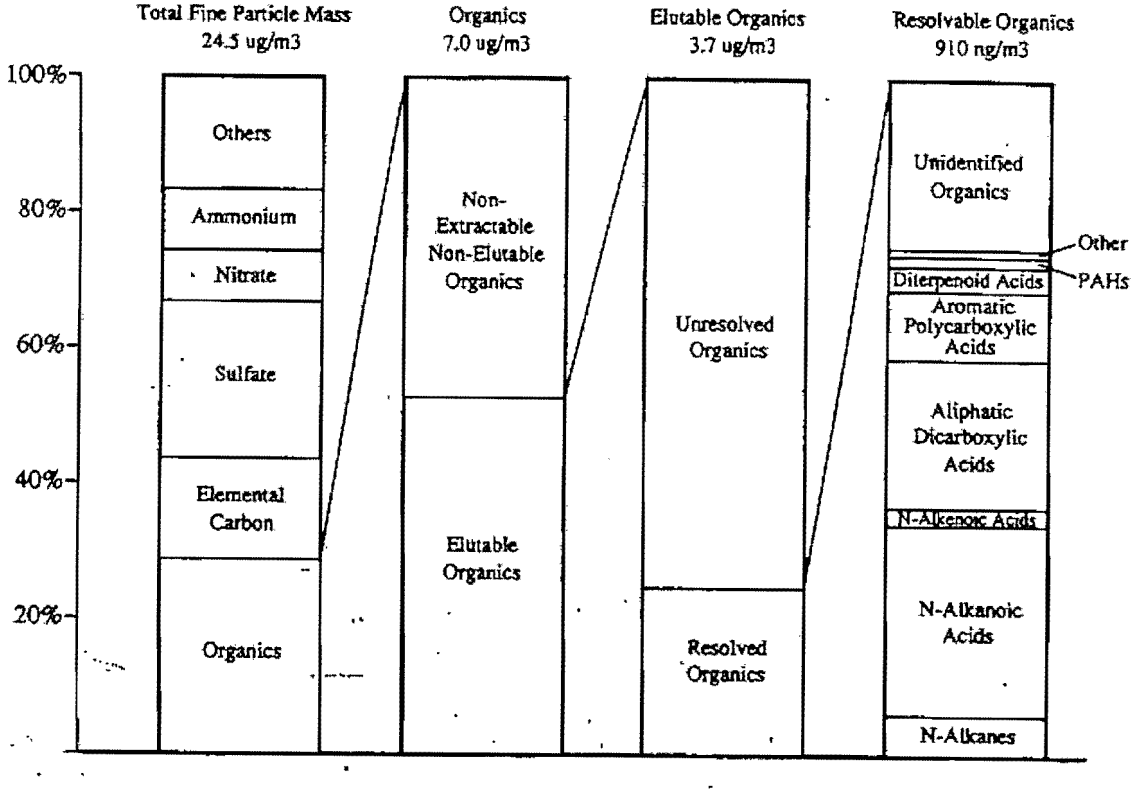


Figure 2.2: *The mass balance on the chemical composition of annual mean fine particulate concentrations of West Los Angeles (Rogge et al., 1993).*

2.1.2. Water soluble organic compounds

WSOC are usually highly polar, oxygenated compounds containing two or more COOH, C=O and/or OH functional groups (Graham *et al.*, 2002). These are aliphatic or oxygenated compounds such as hydroxyamines, amino acids, polyalcohols, sugars, dicarboxylic acids, ketocarboxylic acids and dicarbonyls (Saxena and Hildemann, 1996). WSOC contribute to the ability of particles to act as cloud condensation nuclei (CCN) and are involved in the complex and almost unknown organic liquid phase chemistry of clouds (Fuzzi *et al.*, 2001). The importance of CCN will be discussed in Section 2.1.2.2.

The polar functional groups are responsible for WSOC's high water solubility. The bulk of WSOC can be divided into three classes according to their acid/base characteristics, resulting in (1) neutral compounds, (2) mono- and dicarboxylic acids and (3) polycarboxylic acids (Decesari *et al.,* 2000) as can be seen in Figure 2.3. Mass percentages for the above mentioned three classes were reported as 27%, 32% and 41% respectively, for a specific investigation (Fuzzi *et al.,* 2001). This can however not be generalized.

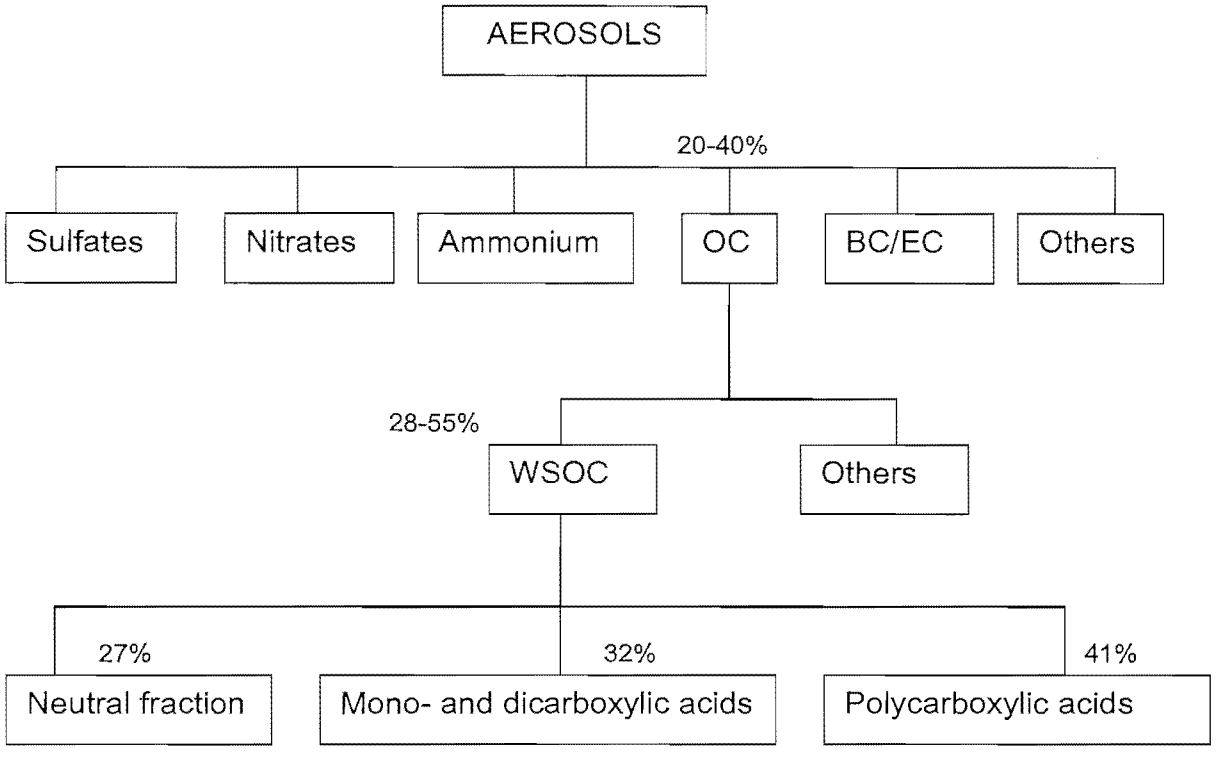


Figure 2.3: *Mass percentages of the composition of aerosols.*

As mentioned in Chapter 1, studies conducted on WSOC within aerosols are still a fairly new research area where most of the studies have been conducted in the northern hemisphere. Thus all the case studies being referred to will be of the northern hemisphere unless otherwise specified.

For every study the environment in which it was being sampled has to be taken into account. For instance, the abundance of WSOC in total carbon (TC) in urban, rural and alpine aerosols has been noted to differ. WSOC accounted for 28-55% of total aerosol carbon content and 1.8-10.7% of aerosol mass in urban Tokyo when a high-volume air sampler with no cut-off rate was used (Sempéré and Kawamura, 1994).

Pöschl (2005) on the other hand studied the $PM_{2.5}$ fraction and derived that the mass concentration of WSOC in total aerosol carbon from various urban, rural and alpine environments were 20±10%; 40±20% and 60±20% respectively. He also found that the macromolecular fraction of WSOC (MWSOC) differed from urban, rural and alpine locations being 30±10%; 50±20% and 40±20% mass concentration fractions of WSOC respectively. Thus the MWSOC account for almost half the mass of WSOC, confirming the notion that the polycarboxylic acid fraction is an important part of the WSOC makeup.

2.1.2.1. Dicarboxylic acids

Previous studies of WSOC in aerosols by GC methods have focused almost exclusively on the characterization of organic acids (Kawamura and Ikushima, 1993). Dicarboxylic acids and especially low molecular weight (LMW) dicarboxylic acids have received much attention because of their potential roles in affecting the global climate (Ho *et al.,* 2006). LMW dicarboxylic acids may have direct and indirect effects on the earth's radiation balance by scattering incoming solar radiation, which counteracts global warming caused by the increase of greenhouse gases. Furthermore LMW diacids can also act as CCN (Ho *et al.,* 2006). Due to the importance of dicarboxylic acids within WSOC and the fact that there is already existing data to compare this study with, this study focused exclusively on dicarboxylic acids as a representative group of WSOC.

The presence of two carboxyl groups makes the diacids less volatile and therefore they are mostly present as particles in the ambient atmosphere (Kawamura and Kaplan, 1987). Total diacids accounted for about 1-3% of the total particulate carbon in the urban areas and even above 10% in the remote marine environment in previous studies (Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1996). Other than direct emissions by vehicles, photochemical processes largely control the atmospheric concentrations of these species (Ho *et al.,* 2006).

Usually a homologous series of normal saturated C_2-C_{12} dicarboxylic acids as well as unsaturated aliphatic (maleic, M and fumaric, F) and aromatic (phthalic, Ph) diacids, have been measured in the past (Kawamura and Yasui, 2005). According to

the theoretical paper of Saxena and Hildemann (1996), C_2-C_9 diacids could account for 4-14% of WSOC. Because photochemical production of diacids is expected to be enhanced by a strong solar radiation and higher ambient temperature, distribution of dicarboxylic acids in the atmosphere showed significant change with the season (Kawamura and Ikushima, 1993). Properties of some dicarboxylic acids can be seen in Table 2.1.

Table 2.1: Properties of C_2-C_{10} dicarboxylic acids as well as Phthalic, Fumaric, Maleic and Malic acid (Fluka and Aldrich Catalogues, CRC Handbook of Chemistry and Physics).

Dicarboxylic acids	Mr	Boiling point	Melting point	Density	Molecular Form
C_2: Oxalic acid	90.04	Sublimes 157°C	188-191°C	1.900^{17} g cm^{-3}	$C_2H_2O_4$
C_3: Malonic acid	104.06	Sublimes	132-135°C	1.619^{10} g cm^{-3}	$C_3H_4O_4$
C_4: Succinic acid	118.089	235°C	187.9°C	1.572^{25} g cm^{-3}	$C_4H_6O_4$
C_5: Glutaric acid	132.12	200°C/20 mm Hg 302°C	95-98°C	1.429^{15} g cm^{-3}	$C_5H_8O_4$
C_6: Adipic acid	146.14	265°C/100 mm Hg	151-154°C	1.360^{25} g cm^{-3}	$C_6H_{10}O_4$
C_7: Pimelic acid	160.17	212°C/10 mm Hg	103-105°C		$C_7H_{12}O_4$
C_8: Suberic acid	174.2	230°C/15 mm Hg	140-144°C		$C_8H_{14}O_4$
C_9: Azelaic acid	188.22	286°C/100 mm Hg 237°C/15mm Hg	109-111°C 100-103°C	6.5 (vs air) **vd**	$C_9H_{16}O_4$
C_{10}: Sebacic acid	202.248	295/100 mm Hg 232/10 mm Hg	130.9°C	1.2705^{20} g cm^{-3}	$C_{10}H_{18}O_4$
C_8: Phthalic acid	166.14	Decomposes	210-211°C	2.18^{191} g cm^{-3}	$C_8H_6O_4$
uC_4: Fumaric acid	116.07	Sublimes 165°C	298-300°C	1.635^{20} g cm^{-3}	$C_4H_4O_4$
uC_4: Maleic acid	116.07	-	137-140°C	1.590^{20} g cm^{-3}	$C_4H_4O_4$
OH-C_4: Malic acid	134.09	-	131-133°C	1.601^{20} g cm^{-3}	$C_4H_6O_5$

2.1.2.2. Cloud condensation nuclei

WSOC and especially LMW dicarboxylic acids are very water soluble with low vapor pressures (Lightstone *et al.*, 2000). Their existence on the aerosol surface therefore alters the chemical and physical properties of the aerosol such as the surface tension and hygroscopic properties. This in turn changes the particle size and cloud condensation nuclei (CCN) activity (Jacobsen *et al.*, 2000) and so enhances the

aerosol's capability to act as cloud condensation nuclei (Kawamura and Usukura, 1993).

Clouds are formed by condensation of water vapor on pre-existing aerosol particles. These pre-existing particles are termed cloud condensation nuclei (CCN) and ice nuclei (IN) (Pöschl, 2005). Aerosol particles containing LMW diacids, even at concentration levels of a few percent, should participate in the CCN process because of the diacids' water solubility and ability to interact with water vapor (Sempéré and Kawamura, 1994). Therefore the diacids in the atmosphere are active CCN and are involved in the in-cloud (rainout) scavenging processes in the upper troposphere (Sempéré and Kawamura, 1994).

An increase in atmospheric CCN and IN concentrations in the atmosphere can have different effects on the formation and properties of liquid water, ice, and mixed-phase clouds and precipitation. Among them are the so-called cloud albedo or Twomey effect (more-numerous and smaller cloud particles reflect more solar radiation), cloud lifetime effect (smaller cloud particles decrease the precipitation efficiency), thermodynamic effect (smaller cloud droplets delay the onset of freezing), and glaciation effect (more IN increase the precipitation efficiency). These and related effects of aerosol, cloud, precipitation, and radiation interactions influence the regional and global radiative energy balance and hydrological cycle, as well as the temperature, dynamics, and general circulation of the atmosphere and oceans (Pöschl, 2005). Moreover, they can promote extreme weather events (intense rain, hail, and thunderstorms) (Waibel *et al.,* 1999).

2.2. SOURCES OF WATER SOLUBLE ORGANIC COMPOUNDS

Sources of WSOC can be either of biogenic or anthropogenic origin. The nature of the source will depend on the location, which can be rural, urban, residential, or marine. One will expect urban atmospheres to be more inclined to anthropogenic pollutants than is the case with rural atmospheres and so the anthropogenic and biogenic input differs from location to location. These biogenic and anthropogenic sources can further be divided into primary emissions and secondary formed aerosols.

Primary anthropogenic dicarboxylic acids come from the direct emission of fossil fuel combustion, such as motor exhausts (Kawamura and Kaplan, 1987) and biogenic biomass burning (Graham *et al.,* 2002). Secondary dicarboxylic acids are formed by the oxidative degradation of anthropogenic or biogenic volatile organic compounds (VOC's) by tropospheric oxidants (Kawamura and Kaplan, 1987). Dicarboxylic acids are largely produced in the atmosphere by secondary photochemical reactions (gas-to-particle conversion); oxidation of hydrocarbons and other organic precursors (Kawamura and Ikushima, 1993).

Although not well documented, it is expected that primary emissions from motor exhausts, as well as combustion from industries, biomass burning and secondary formation due to high temperatures and solar radiation, would be important sources of WSOC in the Vaal Triangle.

2.2.1. Sources of specific dicarboxylic acids

Kawamura and Ikushima (1993) proposed in their study that a source of LMW dicarboxylic acids were anthropogenic gaseous hydrocarbons. Oxalic (C_2), maleic (M), and methylmaleic (mM) acids were said to be produced from the atmospheric oxidation of aromatic hydrocarbons such as benzene and toluene whereas C_4-C_6 dicarboxylic acids were formed from cycloalkenes. By contrast, azelaic acid is said to be of natural origin and can be produced from the oxidation of particulate unsaturated fatty acids containing a double bond at the C_9 position. The higher diacids ($>C_4$) may be partly produced by both homogeneous and heterogeneous reactions of LMW fatty acids, hydroxyl acids and ketocarboxylic acids in the atmosphere (Kawamura and Ikushima, 1993).

2.2.2. Biomass burning aerosols

Vegetation is the major fuel consumed in biomass burning. WSOC concentrations were highest during extreme haze periods associated with burning of pasture sites in the Amazon rainforest (Graham *et al.,* 2002). WSOC accounted for 41-74% of TC. The high WSOC/TC ratios observed highlight the potential for WSOC to be important

in shaping microphysical processes within clouds influenced by smoke aerosols (Graham *et al.,* 2002). Biomass burning WSOC were categorized according to their functional groups into (1) anhydrosugars, (2) sugar/sugar alcohols, (3) aliphatic di-/tricarboxylic acids, (4) aliphatic oxo-/hydroxyacids and (5) aromatic compounds (Graham *et al.,* 2002).

2.2.3. Source strength of anthropogenic and biogenic precursors

The C_3/C_4 and C_6/C_9 dicarboxylic acid mass ratio are useful to understand the production of dicarboxylic acids and the source strength of anthropogenic and biogenic precursors in the atmosphere (Ho *et al.,* 2006).

C_3/C_4 ratio is used as an indication of enhanced photochemical production of dicarboxylic acids in the atmosphere (Kawamura and Ikushima, 1993). Malonic acid (C_3) is derived from the incomplete combustion of fossil fuels or from the secondary atmospheric production. The number 3 is used as an index for secondary formation of dicarboxylic acids (Yao *et al.,* 2004); whereas smaller values are an indication of vehicular exhausts (Ho *et al.,* 2006).

Azelaic acid (C_9) has been proposed as one of the reaction products by ozonolysis of biogenic unsaturated fatty acids (Kawamura and Kaplan, 1987) and adipic acid (C_6) as one of the products by oxidation of anthropogenic cyclohexene (Kawamura and Ikushima, 1993). Thus the C_6/C_9 ratio can be used as a potential indicator to show the strength of biogenic and anthropogenic sources (Ho *et al.,* 2006).

2.3. SINKS OF WATER SOLUBLE ORGANIC COMPOUNDS

Once the aerosols have been emitted to the air or formed in the troposphere, via photochemical oxidation, they undergo physical and chemical aging where after it is only a matter of time before they are scavenged from the atmosphere to fall back to the earth's surface. This fallout from the atmosphere is achieved through dry and wet deposition (sinks). Depending on aerosol properties and meteorological

conditions, the characteristic residence times (life-times) of aerosol particles in the atmosphere range from hours to weeks (Raes *et al.*, 2000).

2.3.1. Dry and wet deposition

Wet deposition refers to rain, snow and fog and dry deposition refers to WSOC still present in aerosols. When considering wet deposition the water soluble organic fraction is referred to as dissolved organic carbon (DOC), whereas the dry deposition's water soluble organic fraction is termed water soluble organic carbon (WSOC) (Sempéré and Kawamura, 1994) or water soluble organic compounds (Kawamura *et al.*, 1996; Ho *et al.*, 2006).

Wet and dry deposition are of importance to determine the molecular distribution of certain species because aerosol samples are usually collected near the ground surface (lower troposphere), whereas the rain droplets and snow flakes scavenge from higher up in the air column including the upper levels of the troposphere (Sempéré and Kawamura, 1994). Due to the fact that dicarboxylic acids are very water soluble and mostly present as particles they may be involved with CCN process and be effectively removed from the atmosphere by in-cloud and below cloud scavenging processes (Sempéré and Kawamura, 1994).

2.3.1.1. Molecular and vertical distribution of water soluble organic compound species

Measuring the molecular distribution and relative abundance of dicarboxylic acids (TC for aerosols and DOC for wet precipitation) in ambient aerosols and wet precipitation samples, may give insight into the physico-chemical processes or vertical distribution of organic compounds in the air column (Sempéré and Kawamura, 1994). During the wet precipitation process aerosol particles are scavenged from the atmosphere. The WSOC fraction should then dissolve in the water droplets, together with gaseous organic compounds and thereby contribute to dissolved organic carbon in the wet precipitation samples (Sempéré and Kawamura, 1994).

When looking at the molecular distributions of dicarboxylic acids, results showed that they are not vertically homogeneous in the air column of the Tokyo troposphere (Sempéré and Kawamura, 1994). Aerosol samples were collected near the ground surface, whereas the rain droplets and snow flakes scavenged the dicarboxylic acids from the air column including upper levels of the troposphere (probably a few hundred meters to a few kilometers above the ground) (Sempéré and Kawamura, 1994). Thus the difference in the molecular distributions of diacids between wet precipitation and aerosol samples may reflect the difference in the diacid distribution in the ground level and upper levels of the troposphere (Sempéré and Kawamura, 1994).

There were generally higher concentrations of C_2-C_9 dicarboxylic acids in wet samples (12-540 $\mu g\ \ell^{-1}$) of Tokyo than in the aerosol samples (1.1-3.0 $\mu g\ m^{-3}$) (Sempéré and Kawamura, 1994) and previous studies showed that diacids were abundantly present in rainwater samples of Los Angeles (Kawamura *et al.,* 1985). The molecular distribution of the ω-oxoacids in both snow and rain samples seemed to be consistent with those of dicarboxylic acids, suggesting that these ketoacids were one of the precursors of dicarboxylic acids (Sempéré and Kawamura, 1994). Time series of rainwater samples showed that the diacid concentrations decreased as a function of time suggesting that dicarboxylic acids were significantly removed from the atmosphere by wet precipitation processes (Sempéré and Kawamura, 1994).

2.4. SECONDARY PRODUCTION OF DICARBOXYLIC ACIDS

Secondary organic aerosol (SOA) components are formed by chemical reaction and gas-to-particle conversion of volatile organic compounds (VOC's) in the atmosphere, which may proceed through different pathways (Pöschl, 2005; Kawamura *et al.,* 1996). Secondary formation and production of dicarboxylic acids is a multi-reaction process and depend on a number of factors (Figure 2.4). In summer the abundance and production of diacids are dependent on the high oxidant concentrations and temperatures, as well as intense solar radiation for photochemical transformation of the primary emitted precursors to take place. In winter photochemical production can be due to an accumulation of the precursors under boundary layers. Secondary

production of water-soluble organic aerosols in Tokyo was found to be more important in the summer than in winter, with a concentration maximum during the day (Kawamura and Yasui, 2005).

Non-methane hydrocarbons (NMHC's) were an important source for the secondary production of diacids and related water-soluble organic compounds via gas-to-particle conversion in the urban Tokyo atmosphere during a summer season (Kawamura and Yasui, 2005). Because the production of oxidants are associated with increase in solar radiation, this suggested that the origins of diacids were largely involved with secondary photochemical processes in the atmosphere rather than primary emissions from automobiles, although they were the major sources of the precursors for bi-functional organic acids and aldehydes (Kawamura and Yasui, 2005).

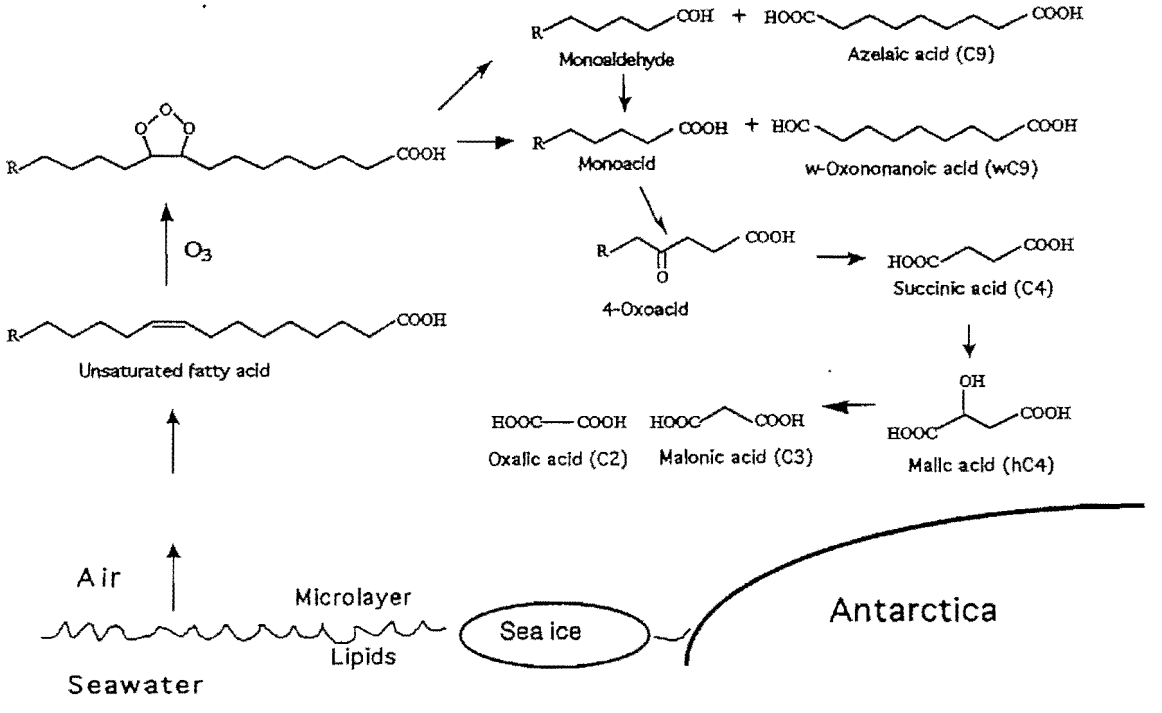


Figure 2.4: *A proposed reaction scheme for the secondary production of succinic acid and other low molecular weight dicarboxylic acids from unsaturated fatty acids in the atmosphere of the Southern Ocean and Antarctica (Kawamura et al., 1996).*

2.5. SUMMER AND WINTER DICARBOXYLIC ACID CONCENTRATIONS

Whether dicarboxylic acid concentrations are more pronounced in summer or winter can differ depending on location and meteorological conditions. Mid-latitude dicarboxylic concentrations of Tokyo showed a diurnal distribution with a daytime maximum and an increase in the summer (Kawamura and Yasui, 2005); whereas in Hong Kong the relative abundances of diacids differed from winter to summer with some diacid concentrations being higher alternatively in winter and summer (Ho *et al.*, 2006).

In the summer of 1988-1989 total suspended particles (TSP) were measured in Tokyo and delivered diacid concentrations which were higher than the concentrations in winter. This was due to higher temperatures, higher oxidant levels in the atmosphere and enhanced solar radiation which all promotes the secondary production of dicarboxylic acids by photochemical oxidation of precursor organic species (Kawamura and Ikushima, 1993). When, however, the winter dicarboxylic acid concentrations were higher than that of the summer's, it was usually caused by the accumulation of pollutants under inversion layers which enabled secondary formation of acids to take place (Kawamura and Ikushima, 1993).

With the study of 2003 conducted in Hong Kong the diacid concentrations of $PM_{2.5}$ samples were higher in winter except for a few exceptions (C_6, C_8, C_{11}, C_{12}, F, and Ph), which were higher in the summer. Hong Kong is a warm, humid and cloudy coastal city and vehicular emissions are the major primary local air pollutants. High concentrations are usually observed in the winter due to the frequent development of stagnating high-pressure systems and inversion layers in the lower atmosphere as well as less chance of precipitation in winter (Ho *et al.*, 2006). What further possibly contributed to the lower summer concentrations could have been the mixing of air and dilution of polluted air by the inflow of air mass from the coast; or possible rainfall that washed out the expected high concentrations (Ho *et al.*, 2006). Thus depending on meteorological conditions and primary emissions, dicarboxylic acid concentrations could be either higher in winter or in summer.

2.5.1. Diurnal distribution

To obtain a diurnal cycle of dicarboxylic acids a 3 hour interval sampling campaign was undertaken in Tokyo by Kawamura and Yasui, 2005. Throughout the 3 hour sampling periods, it was observed that concentrations of diacids significantly varied by factor 3-5, showing a maximum at around noon. Furthermore a dynamic change in the molecular composition of organic acids within a day was also observed. Total concentrations of diacids increase from the lowest values in night time (2-5 am) to the highest values in daytime around 8 am to 11 am or at noon (Kawamura and Yasui, 2005). The following observations were made:

2.5.1.1. Early morning

The relative abundance of total diacids increased from midnight (0.2% at 2 am to 5 am) toward noontime (1% at 11 am to 2 pm). A rapid increase in the relative abundance in the morning again supports the photochemical production of dicarboxylic acids theory. Interestingly, the relative abundances had been higher in the summer than in the winter and are consistent with elevated solar radiation in summer by ca. 50% for 11 am to 2 pm.

2.5.1.2. Afternoon

After the daytime maximum, concentrations of total diacids had decreased toward the late afternoon and night. It could be suggested that photochemical production of diacids had been cancelled out by the atmospheric scavenging either by decomposition or deposition taking place during the afternoon. Alternatively, such a decrease could have been caused by the expansion of planetary boundary layers in the afternoon and thus subsequent vertical mixing of the air.

Interestingly, summer samples had shown a continuing increase of diacid-C/TC ratios in the afternoon and this had been mainly due to the production of small diacids (C_2-C_4) via further oxidation of some intermediate compounds produced by the oxidation of hydrocarbons (Kawamura et al., 1996a). Due to the fact that

oxidants were still high (>20 ppb) in the late evening of summer, oxidation of organic precursors had likely occurred even in the darkness. The secondary production of diacids, especially C_2, C_3 and C_4 had possibly overwhelmed their degradation or deposition in the late afternoon.

2.5.1.3. Night time

A decrease in dicarboxylic acid concentrations at night could be contributed to a positive uptake of water vapor by aerosol particles or quartz filters if relative humidity increased significantly at night. This can be seen from the sharp increase in the diacid/aerosol mass ratio from 2 am to 5 am and 5 am to 8 am and could have been caused by the enhanced relative humidity exceeding 90%.

2.5.1.4. Specific dicarboxylic acids

Individual compound-C/TC ratios had shown a different trend among diacids although most species had peaked at 11 am to 2 pm. Small diacid-C/TC ratios such as C_2, C_3 and C_4 had increased in the late evening whereas phthalic acid (Ph) had shown a sharp drop in the afternoon and stayed low well into the night. Such a difference in the diurnal distributions could have been caused by a difference in their precursors and/or formation mechanisms. Normal saturated C_2-C_4 diacids are produced from more common precursors including unsaturated and saturated hydrocarbons, monocarboxylic acids, aldehydes, ketoacids, etc. In contrast, unsaturated and branched-chain diacids have been considered to generate via photochemical oxidation of more specific precursors such as aromatic hydrocarbons and methylcycloalkenes (Kawamura *et al.*, 1996a).

2.6. RELATIVE ABUNDANCE OF DICARBOXYLIC ACIDS

As mentioned before a homologous series of normal saturated C_2-C_{12} dicarboxylic acids, as well as unsaturated aliphatic (maleic and fumaric) and aromatic (phthalic)

diacids are usually measured when WSOC studies have been undertaken (Kawamura and Yasui, 2005). In atmospheric aerosols oxalic acid (C_2) were generally the most abundant diacid, followed by malonic (C_3) or phthalic acid (Ph) and fourth succinic acid (C_4) (Ho *et al.,* 2006). In Table 2.2 some dicarboxylic acids and their abundance is listed using different methods. In all the samples the *cis* configuration (maleic acid, M) were more abundant than the *trans* configuration (fumaric acid, F) (Kawamura *et al.,* 1996). The predominance of *cis* configuration could be associated with the chemical structure of the precursor compounds (unsaturated hydrocarbons) (Kawamura and Ikushima, 1993).

Although the total dicarboxylic acids increase with an increase in atmospheric ozone concentrations, the degree of increase is dependent on the carbon chain length and structure of the diacid species (Ho *et al.,* 2006). Abundance of the individual dicarboxylic acid species decreases with an increase in carbon chain length, although adipic (C_6) and azelaic acids (C_9) are relatively abundant (Ho *et al.,* 2006). Better correlations are usually found between the smaller diacids (C_2-C_4) and ozone (Ho *et al.,* 2006).

Table 2.2: A comparison of dicarboxylic acids analyzed with different methods in literature (Ho *et al.*, 2006).

Average concentrations (ngm^{-3}) of selected dicarboxylic acids in the literature										
Site/type	**Season**	**Size**	**Method**	**Oxalic**	**Malonic**	**Succinic**	**Adipic**	**Azelaic**	**Methylmaleic**	**Phthalic**
Tokyo, Japan/Urban[a]	One year average	TSP	GC-MS/FID	270	55	37	16	23	3.8	15
Vienna, Austria/Urban[b]	Summer	TSP	GC-MS/FID	340	244	117	117			18
Christchurch, New Zealand[c]	Winter	PM10	IC	85	6.6	31				
	Summer	PM10	IC	39	5.1	23				
Leipzig, Germany/Urban[d]	Summer	TSP	IC	229	66	35				
Houston, USA/Urban[e]	Summer	PM2.5	GC-MS/FID		12.5	16.1	6.9	12.5		
Shangai, China/Urban[f]	One year average	PM2.5	IC	500	40/100	200				
Beijing, China/Urban[f]	One year average	PM2.5	IC	300	100	30/20				
Beijing, China/Urban[g]	Summer and winter	PM2.5	CE	218	39	39				
Nanjing, China/Urban[h]	Winter	PM2.5	GC-MS/FID	880	114	146	24	92		
	Spring	PM2.5	GC-MS/FID	440	63	80	49	195		
Poly U, Hong Kong/Urban[I]	Summer	PM2.5	IC	90	13	7				
	Winter	PM2.5	IC	350	20	50				
Hok Tsui, Hong Kong/Remote[I]	Summer	PM2.5	IC	40	ND	ND				
	Winter	PM2.5	IC	370	20	60				129
Seven locations, Hong Kong[J]	Autumn and winter	TSP	GC-MS	1084	142	118				
Arctic/Remote[k]	One year average	TSP	GC-MS/FID	13.6	2.46	3.73	0.82	0.26		1.5
Sevettijarvi, Finland/Remote[L]	Two year average	PM15	IC	8.6	1.5	2.9	27.3	148		1.1
Pacific Ocean/Marine[m]	Autumn and winter	TSP	GC-MS/FID	40	11	2.8	2.1	0.57	0.034	0.66
Hong Kong roadside/Urban[n]	Winter	PM2.5	GC-MS/FID	478	89.1	71.9	10.7	16.8	6.4	78
	Summer	PM2.5	GC-MS/FID	268	47.6	33	12.7	9.06	6.57	89.9

[a] Kawamura and Ikushima (1993)
[b] Limbeck and Paxbaum (1999)
[c] Wang and Shooter (2004)
[d] Rohrl and Lammel (2001)
[e] Yue and Fraser (2004)
[f] Yao *et al.* (2004)
[g] Huang *et al.* (2005)
[h] Wang *et al.* (2002)
[I] Yao *et al.* (2004)
[J] Li and Yu (2005)
[k] Kawamura *et al.* (1996b)
[L] Ricard *et al.* (2002)
[m] Kawamura and Sakaguchi (1999)
[n] Ho *et al.* (2006)
ND (not detected)

2.7. METHODS USED TO STUDY WATER SOLUBLE ORGANIC CCOMPOUNDS

Technology has developed over the years in so far that today we have state of the art analytical equipment to analyze and quantify any chemical compounds with. However, as mentioned before; the compounds being sought govern the choice of the analytical method and signal processing procedures (Saxena and Hildemann, 1996).

There are currently two prominent methodologies to analyzing WSOC:

(1) An individual compound approach as performed by Kawamura and Ikushima (1993) mainly using GC-MS analysis (discussed in Paragraph 2.7.1).

(2) The classifying of WSOC as a whole as was done by Decesari et al. (2000) mainly using H^1-NMR (discussed in Paragraph 2.7.2).

Although ion chromatography (IC) has not received much attention for WSOC analysis it is also discussed (Paragraph 2.7.3), since it has numerous advantages.

2.7.1. Gas chromatography - mass spectroscopy

To date, GC-MS has been the method of choice for characterizing individual organic compounds within aerosol samples, primarily because of its high sensitivity and resolving power (Jacobsen *et al.,* 2002). GC-MS is the most common tool for investigating the molecular composition of aerosol OC after single or multiple organic solvent extractions of samples (Rogge *et al.,* 1993). Characterization of polar compounds by GC-MS though requires that they first be derivatized, i.e., converted to less polar compounds, so that they will elute through a GC column (Graham *et al.,* 2002). But derivatization and the type of derivatization agent being used, is aimed at a specific type of polar functional group (Saxena and Hildemann, 1996). A typical chromatogram can be seen in Figure 2.5. However, in these methods a substantial portion of polar oxygenated organic compounds, specifically the more water-soluble ones, remain unanalyzed (Decesari *et al.,* 2000).

Even if the solvent extraction is efficient in terms of recovery of total OC, the resolution of the complex mixture containing a wide range of different organic

molecules is still inefficient, and the individual component approach normally ends up accounting for only a few percent of the total WSOC composition (Decesari *et al.,* 2000).

Functional group analyses performed by spectroscopic techniques such as nuclear magnetic resonance (NMR) on the other hand also have a major drawback to the characterization of complex mixtures of organic species. As in the case of atmospheric aerosols, they do not allow one to attribute the functional group detected to a particular molecule or to specify molecules carrying more than one functional group (Decesari *et al.,* 2000). Thus for the purpose of identifying which functional group belongs to which molecule or species, using GC-MS in combination with NMR results in better characterization.

The following is a literature based methodology from Kawamura and Ikushima (1993) as followed in GC-MS analysis of WSOC's.

The organic acids collected on the filters are determined through a three step procedure:

a) Extraction of WSOC's collected on a membrane filter, by using a hydrophilic solvent;
b) Derivatization of free acids with diazomethane or a BF_3-alkanol complex, leading to alkanoic esters;
c) Analysis of the eluent by capillary high resolution Gas Chromatography-Mass Spectrometry (HRGC-MS).

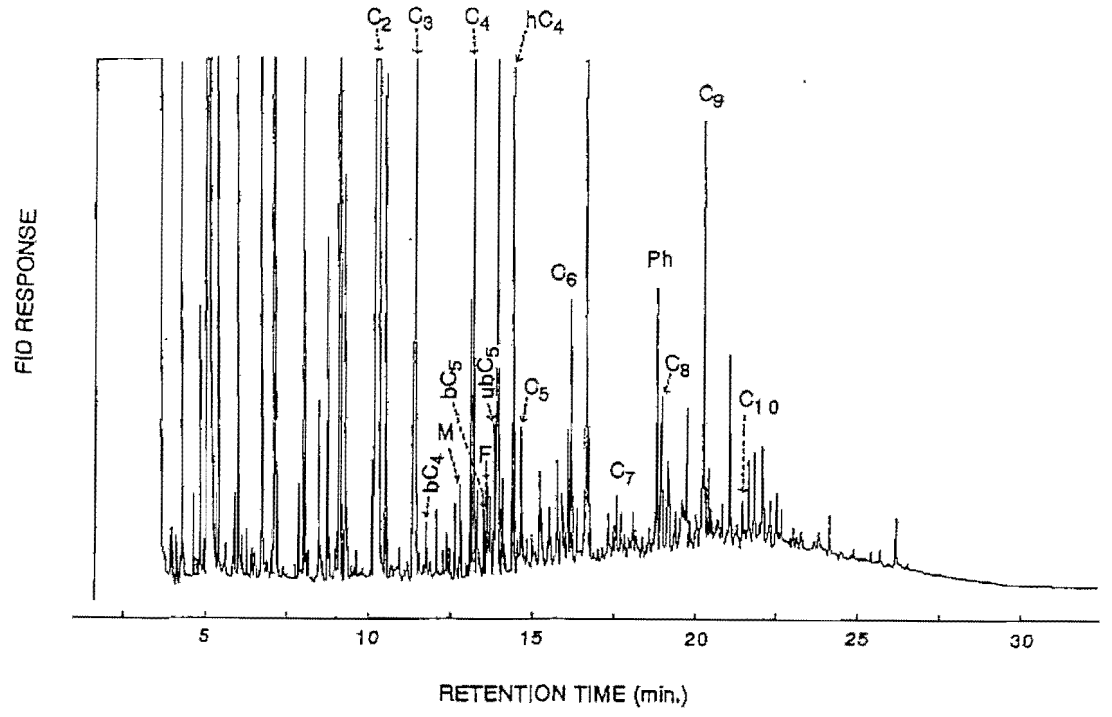


Figure 2.5: *A GC-FID chromatogram of short chain dicarboxylic acids (Kawamura and Ikushima, 1993).*

2.7.2. Proton nuclear magnetic resonance, ion exchange chromatography and total organic carbon

Instead of attempting an investigation of WSOC at the molecular level, an approach that is usually able to account for only a small fraction (10-15%, Rogge *et al.,* 1993), this methodology utilizing ion exchange chromatography (IEC), proton nuclear magnetic resonance (H^1-NMR) and total organic carbon (TOC) identifies and quantifies WSOC into a number of compound classes (Decesari *et al.,* 2001). According to this procedure, the complex mixture of WSOC can be separated into three main classes of compounds: (a) neutral/basic compounds; (b) mono- and dicarboxylic acids; (c) polycarboxylic acids. The samples are then further analyzed by H^1-NMR spectroscopy (Decesari *et al.,* 2001).

The H^1-NMR spectra mainly consist of very broad, poorly resolved peaks, deriving from the overlap of a very large number of individual minor contributions (Decesari *et al.,* 2001) as can be seen in the H^1- NMR chromatogram of Figure 2.6. The four

most representative categories of functional groups were identified from H^1-NMR spectra: (1) aromatic compounds, (2) aliphatic groups bound either to carbonyls and/or other unsaturated structures, (3) alcohols and ethers, and (4) aliphatic chains (Decesari *et al.,* 2000). While the proposed characterization methodology supplies a less detailed picture compared to individual compound speciation, the more comprehensive and synthetic data would probably be well suited for modeling purposes (Decesari *et al.,* 2001).

The aerosol water extracts are first analyzed by H^1- NMR spectroscopy before chromatographic separation to obtain preliminary information on the main functional groups present (Decesari *et al.,* 2000). Aqueous samples are usually separated by high-performance liquid chromatography (HPLC) in reverse-phase mode, but very polar compounds are not retained by the reverse-phase columns (Gundel *et al.,* 1993). More suitable techniques for the fractionation of WSOC are ultrafiltration (UF), size exclusion chromatography (SEC) and ion exchange chromatography (IEC). IEC is a good choice if carboxylic acids are the main class of organic compounds in the water-soluble fraction of atmospheric aerosol (Gundel *et al.,* 1993). In this method the overall recovery of WSOC, obtained by summing the carbon content of the three fractions separated by the chromatographic procedure and comparing the sum with the carbon content of the bulk sample, is 77%. The apparent loss of 23% of WSOC in the fractionation procedure was due to several concurrent reasons: compounds irreversibly adsorbed on the column, losses in the freeze-drying procedure, losses due to acidification of the samples before TOC analysis (Decesari *et al.,* 2000).

Importantly, this approach is not alternative to the classical speciation methods aimed at identifying individual compounds. On the contrary, this suggested approach can provide helpful guidance for the individual compound speciation techniques. Though this approach supplies a less detailed picture compared to the individual compound speciation, it certainly provides more comprehensive and useful information for modeling purposes and is particularly helpful when aerosol chemical mass closure is pursued (Decesari *et al.,* 2000).

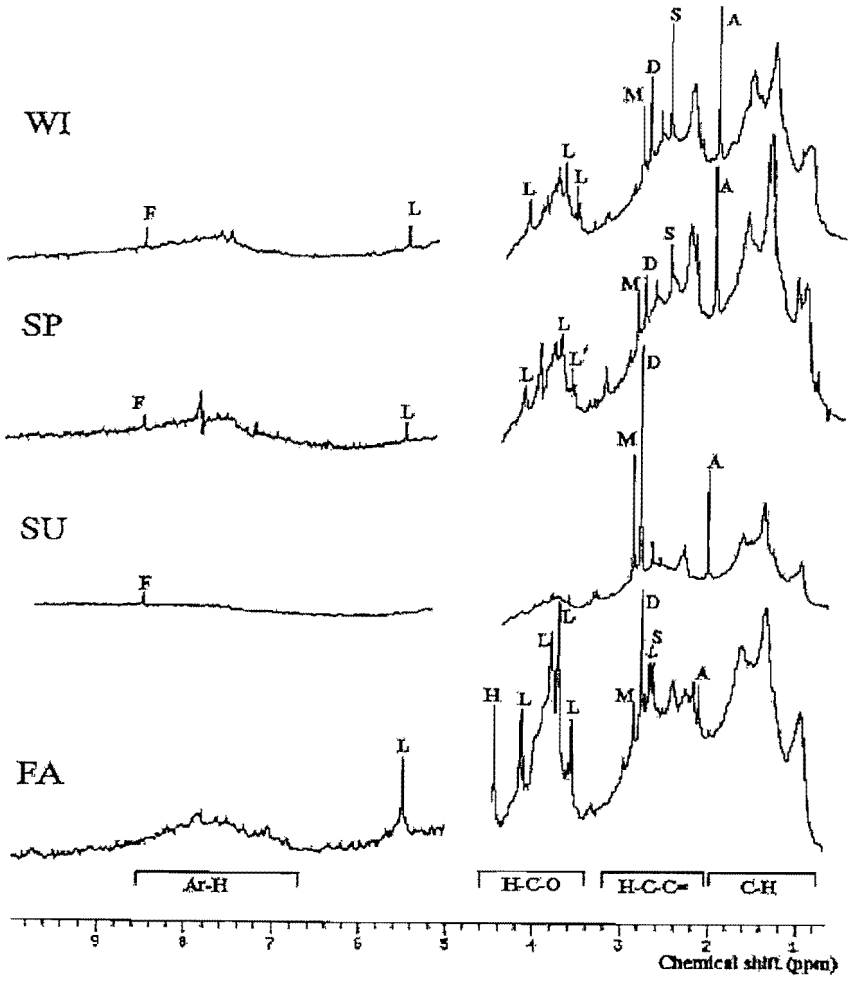


Figure 2.6: *H^1 -NMR analysis of WSOC fraction from annual aerosol samples (Decesari et al., 2001).*

2.7.3. Ion chromatography

Analysis of WSOC can entail a lot of chemical methods such as extraction and derivatization, but these methods can be time consuming, labor intensive and error prone as stated in section 2.7.1. As an alternative, IC offers tremendous advantages by being free from the interferences that plague wet chemistry, and offers superior sensitivity, accuracy and dynamic range. IC is a fast and versatile system that can identify and quantify multiple ions in minutes, thus effectively shortening the analytical time. With chemical suppressors even complex samples can be analyzed by direct injection, with little or no sample preparation (Small and Bowman, 1998).

IC using ion exchange chromatography can sufficiently analyze organic acids including mono- and dicarboxylic acids (Amati *et al.,* 1999). IC like the GC-MS is a powerful and sensitive technique for identifying individual compounds (Figure 2.7). It analyzes either in the cation or anion mode and for this purpose no derivatization or intensive extraction of samples is necessary. The analytes one wishes to analyze only has to be dissolved in the aqueous phase for the IC to detect them either in the anion or cation mode. With the case of WSOC and specifically dicarboxylic acids, the IC is operated in the anion phase. This is a simple, sensitive and effective method that is much less time consuming to analyze for WSOC. Ion chromatography (IC) is widely used for the measurement of inorganic ions in particles, since it offers advantages in terms of sensitivity and multiple analyte determination in a single assay (McMurray, 2000).

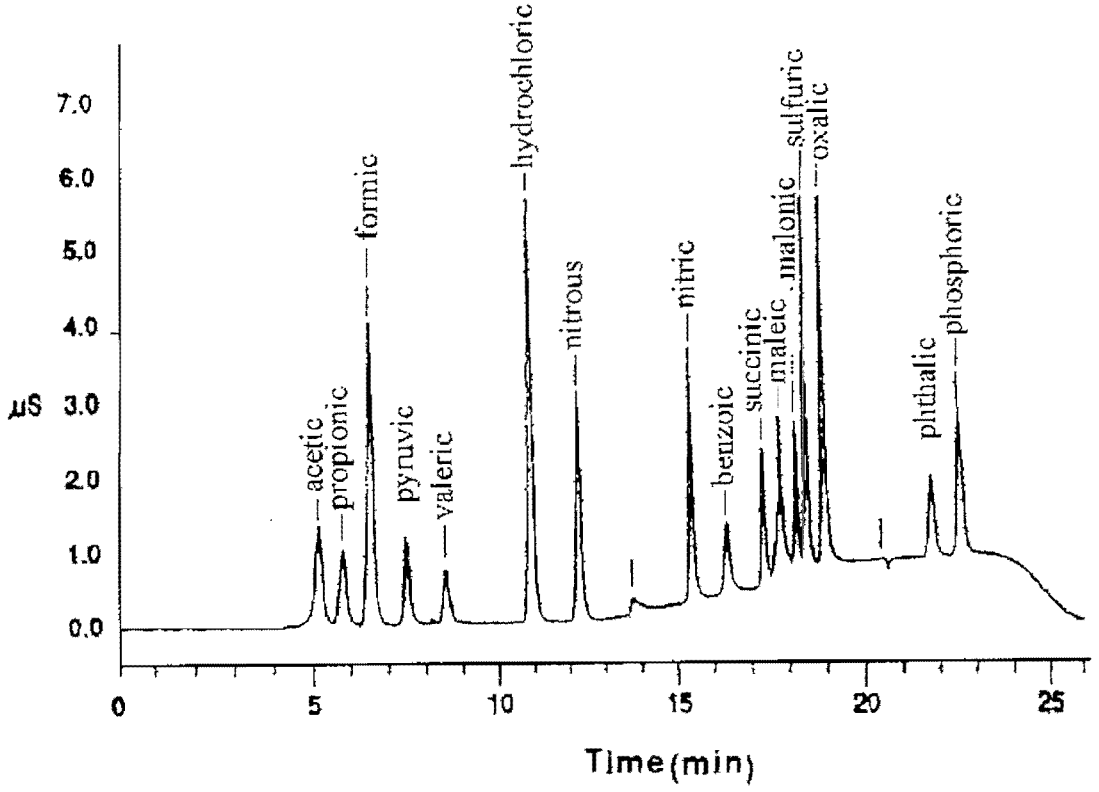


Figure 2.7: *IC chromatogram of organic acids (Amati et al., 1999).*

2.8. GAPS IN CURRENT KNOWLEDGE

WSOC is currently still a new research area and any data that can be obtained is essential for WSOC inventories and elucidating aerosols as a whole. South Africa is a growing and developing country with no studies on WSOC documented in the open literature. The fact that only a few studies have yet been done in the southern hemisphere also makes this study very important. The expectation though is that the results will differ from that of the northern hemisphere due to different climatic conditions (such as rain and wind patterns in summer and winter) and pollution sources.

Experimental studies test, explicitly or implicitly, *a priori* hypothesis about the molecular composition: the compounds being sought govern the choice of the analytical method and signal processing procedures (Saxena and Hildemann, 1996). However, detection and studying of WSOCs are sometimes difficult due to limitations of analytical techniques and there is never one technique to elucidate all the WSOC's. A series of techniques thus has to be used in conjunction with each other. Previous studies have applied either GC-MS or IC as analytical techniques for the analysis of dicarboxylic acids. In this study both these techniques will be used to detect and quantify selected dicarboxylic acids.

CHAPTER 3
EXPERIMENTAL PROCEDURES

In this chapter the study area and the sampling sites are discussed. The sampling procedure and equipment as well as the analytical techniques used are also described.

3.1. GEOGRAPHY AND METEOROLOGY OF THE VAAL TRIANGLE

Historically the Vaal Triangle, which is situated in the Highveld, includes an area stretching from Randvaal in the north to Sasolburg in the southwest and Deneysville in the east (Figure 3.1). The towns of Vereeniging, Vanderbijlpark and Meyerton fall within this geographic area with various low income settlements such as Boipatong, Bophelong, Evaton, Orange Farm, Sebokeng, Sharpville and Zamdela also included. The area spans approximately 3600 km^2, extending across both the Free State and Gauteng provinces and is contained within two district municipalities namely Northern Free State and Sedibeng. Based on the 2001 census, the population of the Vaal Triangle Priority Air-shed was estimated to comprise a total population of 2,532,362. Elevation across the Vaal Triangle is relatively uniform, with elevations of approximately 1550 m in the east, decreasing slightly to 1452 m above mean sea level in the west. The Vaal River runs through the region and forms the natural boundary between the Gauteng and Free State Province (VTPA AQMP Baseline Report, 2007).

The natural veld type of the Vaal Triangle is classified as *Cymbopogon-Themeda*, characteristic of regions with rainfall between 500 and 700 mm per annum, and very cold winters. Over 80% of the rainfall occurs during the October to March period, with rainfall mainly occurring as sudden downpours and thunderstorms. Summer months experience on average 10 to 14 rain days a month, with only 1 to 2 rain days occurring during winter months. The annual average number of rain days is given as 88 based on the long-term record for Vereeniging (1951-1984) (VTPA AQMP Baseline Report, 2007).

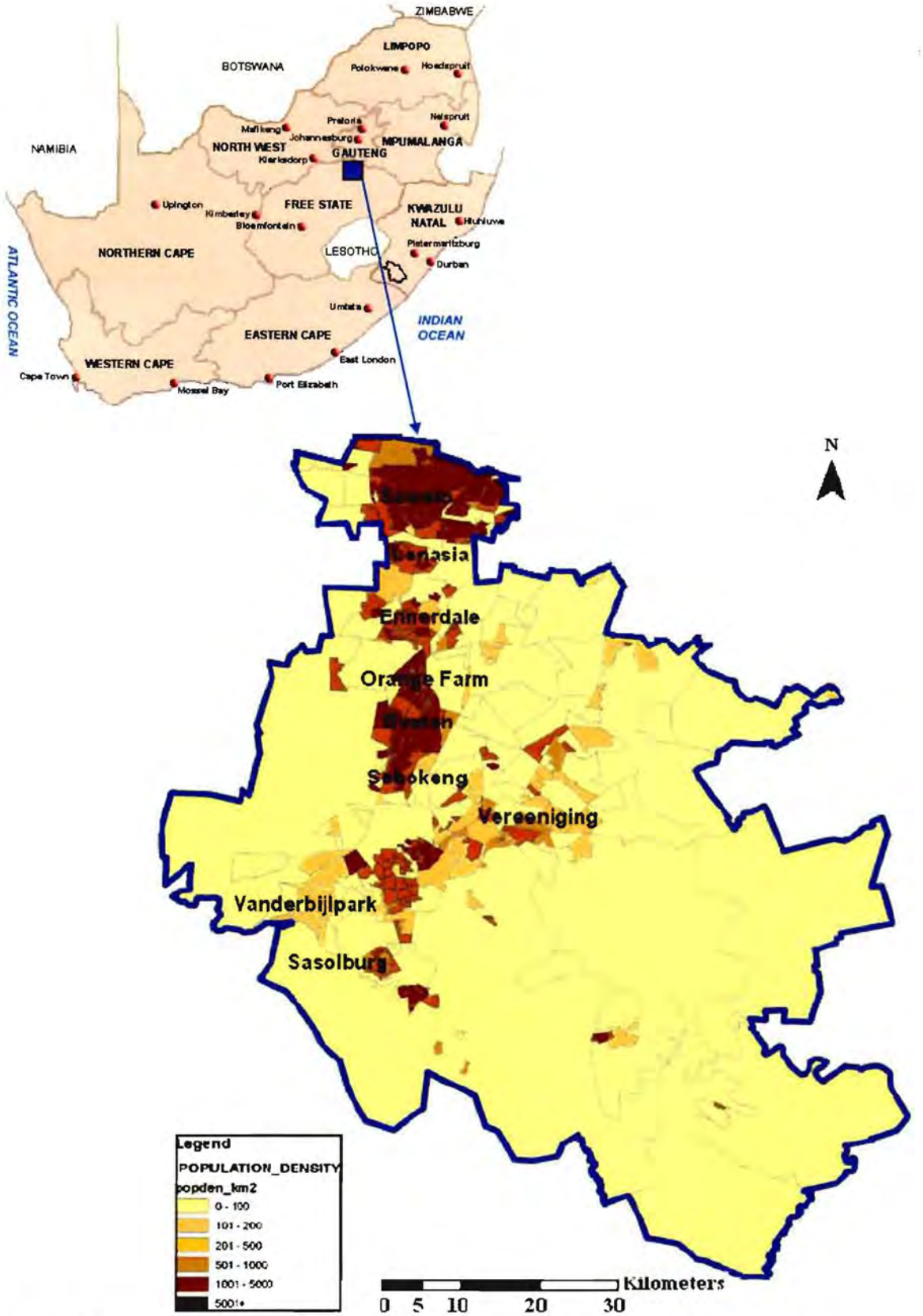


Figure 3.1: *Population density of the Vaal Triangle Air-shed Priority Area based on 2001 Census data (VTPA AQMP Baseline Report, 2007).*

Temperatures are moderate, for instance for Vereeniging the reported annual maximum, minimum and mean temperatures were 23.9°C, 9.1°C and 16.6°C respectively based on the long-term averages (1903-1984) (Schulze, 1986). Average daily maximum temperatures ranged from 27.8°C in January to 17.7°C in July, with daily minimum ranging from 15.5°C in January to just above 0°C in June and July (Schulze, 1986).

The Vaal Triangle encompasses a mixture of commercial, agricultural, and residential land use activities, all within close proximity to one another. Beyond the borders of the urban areas, the land is considered to be semi-rural and is used for low intensity farming practices. The soil in this region is generally sandy; however, where the soil is deep enough conditions are more suitable for the farming practices, such as cultivation or grazing (VTPA AQMP Baseline Report, 2007). Industrial activities within this region include coal fired power stations, chemical factories, petrochemical plants, metallurgical plants and multiple small industries (Scorgie *et al.*, 2004).

Wind patterns and pollution transport from the Highveld were modelled by forward trajectory analysis from which five categories of transport were identified (VTPA AQMP Baseline Report, 2007). The breadth of the arrows in Figure 3.2 gives an indication of the spatial variation of the transport pathway, but not the amount being transported. The five transport categories are best identified as transport plumes and were: the Indian Ocean plume, the recirculation plume, the Atlantic Ocean plume, the African plume and the Southern Ocean plume. The most frequently occurring of the five types were the Indian Ocean plume (48 %) in which material were transported directly from the Highveld to the Indian Ocean; or to it after initially moving westward before recurving anticyclonically to the south east in a swath to exit over Ben Macdhui (Lesotho Highlands). The second most important plume was the recirculation plume (32 %). Together, the Indian Ocean and the recirculation plumes transported 80 % of material to the south-east and toward Australasia. The Atlantic Ocean plume transported ~ 14% of the air from the Highveld to the Atlantic Ocean. About 4% were transported north of 10°S to the equator and lastly about 2% were transported directly south into the high latitudes in the Southern Ocean plume (VTPA AQMP Baseline Report, 2007).

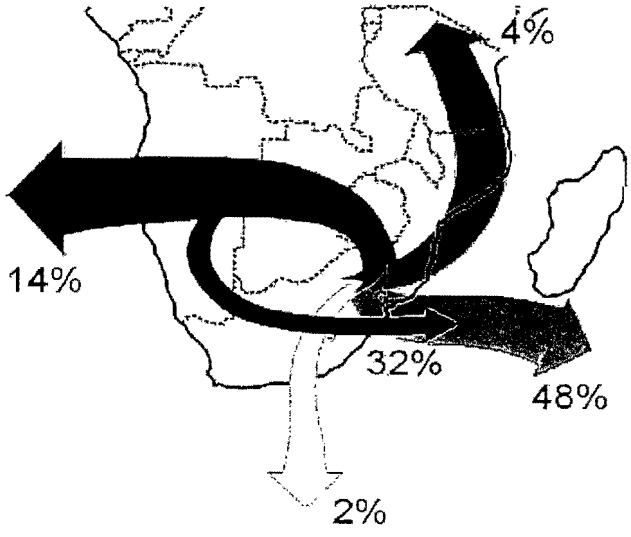


Figure 3.2: *Five transport pathways identified from the forward trajectory analysis for the five-year period 1990-1994 (VTPA AQMP Baseline Report, 2007).*

The wind direction in Vereeniging is dominated by an in-flow from the north and north-north-west and the influence of the prevailing anti-cyclonic circulation over the continent is clearly evident. Wind speeds are generally low to moderate which reduces the potential for the dispersion and dilution of air pollution (DEAT VAPA Draft Siting Report 2006). The trans-boundary transports of pollutants from areas which fall outside a sampling area also play an important role. The transport of emissions from the Alrode industrial area in Gauteng is anticipated to influence the ambient air quality in the Vaal Triangle area (DEAT VAPA Draft Siting Report 2006).

Another characteristic of South African air is the occurrence of stable layers in the early mornings and in winter time. The frequent, persistent and the spatially-continuous occurrence of absolutely stable layers of air are confined features of the Southern African atmospheric environment. The elevated layers occur preferentially at ~850 hPa (over the coastal regions only), ~700 hPa, ~500 hPa and ~300 hPa throughout the troposphere. They are highly effective in acting as upper air boundaries that control the free diffusion of aerosols and trace gases (including water vapor) vertically and may have repercussions on scales ranging from local to synoptic (Freiman and Tyson, 2000). Elevated PM_{10} concentrations are frequently recorded during the winter months of May to August and are due to an increase in domestic fuel burning and poor atmospheric dispersion potentials during these

months. These elevated concentrations coincided with periods of low temperatures and stable atmospheric conditions as is common during winter months (VTPA AQMP Baseline Report, 2007). Thus the prevailing meteorological conditions in an area have a major influence on the dispersion and dilution of pollution of atmospheric pollutants in the Vaal Triangle area (DEAT VAPA Draft Siting Report 2006).

3.2. SAMPLING SITES WITHIN THE VAAL TRIANGLE

Elevated concentrations of particulate concentrations are known to occur in the Vaal Triangle. Particulate emissions from domestic coal and wood burning have been identified as the major cause of poor ambient air quality and have a significant adverse impact on human health (VTPA AQMP Baseline Report, 2007). Significant and potentially significant industrial emitters within the Vaal Triangle are grouped within the larger industrial areas within Vanderbijlpark, Vereeniging, Sasolburg and Meyerton. For the purpose of this study three sampling sites, (1) Three Rivers (representing Vereeniging), (2) Vanderbijlpark and (3) Sasolburg were chosen to be representative of the situation in the Vaal Triangle. The sampling sites were situated in a residential (Three Rivers, Vereeniging), and urban (Vanderbijlpark, metallurgic industries; Sasolburg, petrochemical industries) environment of the Vaal Triangle. The geographic distribution of the sites can be seen in Figure 3.3. Sampling was done at the three specified sites during July 2006 and March 2007. This was done in order to obtain winter and summer data.

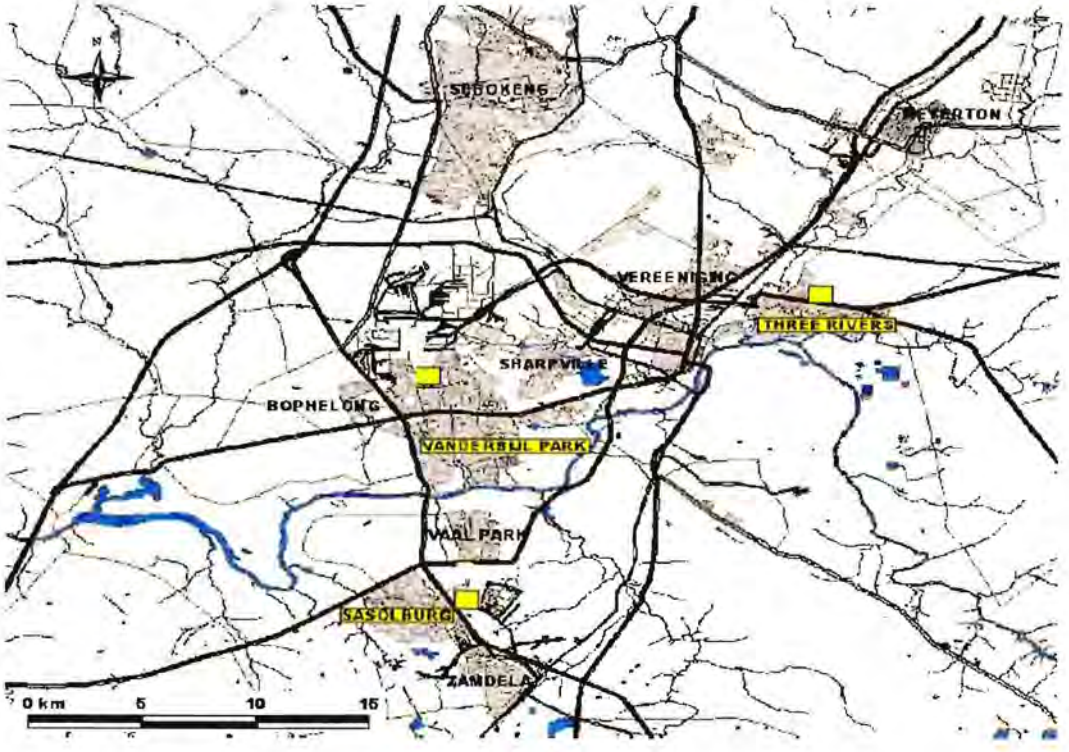


Figure 3.3: *Geographic position of the sampling sites in the Vaal Triangle. (Monitoring sites are indicated by the yellow squares).*

3.2.1. Vereeniging

According to the Department of Environmental Affairs and Tourism, the main contributing sources of particulate matter in Vereeniging include: Mittal Vereeniging (Vaal Works), Rand Water Board and the New Vaal Colliery. Other sources include Brickveld Stene, SCAW, Coverland Roof Tiles and Lime Distributers (VTPA AQMP Baseline Report, 2007).

The location of the Three Rivers sampling site in Vereeniging for July 2006 and March 2007 (Figure 3.4) was at 26°39'14.21"S latitude and 27°59'24.01"E longitude. Three Rivers is a residential area of Vereeniging with no major industries in the area. Therefore the site can be classified as a residential site, with the main contributing sources expected to be traffic and household related.

Figure 3.4: *The Three Rivers sampling site (Vereeniging) with the MiniVol samplers on the roof.*

3.2.2. Vanderbijlpark

According to the Department of Environmental Affairs and Tourism, the main contributing sources of particulates in Vanderbijlpark include: Mittal Steel Vanderbijlpark, Vitro Building Products and Davesteel (Cape Gate). Other potentially significant sources include Africa Cables, Dorbyl Heavy Engineering and Slagment. Potentially significant sources that have not been quantified include Heckett Multiserv, Sharon Wire Mill, Van Riels Stene and Zeekoeistene (VTPA AQMP Baseline Report, 2007).

The location of the July 2006 site (Figure 3.5) was at 26°41'16.61"S latitude and 27°49'8.21"E longitude. The site was situated in a field, used at the time for sporting activities. The site could unfortunately not be used during March 2007, since the ground on which the site was located had been sold for housing development. Therefore, an alternative site which was close in proximity to that of the July 2006 site was selected. The location of the March 2007 site was at 26°41'6.10"S latitude and 27°48'48.63"E longitude. A photo of this sampling site is unfortunately not displayed.

The Vanderbijlpark sites could be classified as semi-industrial due to their close proximity to the central business district (CBD) which features main industries as well as various other businesses. Consequently traffic emissions could also be expected to contribute greatly to the atmospheric particle formations. The March 2007 site was situated close to informal settlements, which could be expected to be a significant contributor of biomass and coal burning.

Figure 3.5: The *Vanderbijlpark site used during July 2006: MiniVol samplers are on the roof of the sampling station.*

3.2.3. Sasolburg

According to the Department of Environmental Affairs and Tourism, the main significant contributing sources of emissions in Sasolburg include: the Sasol Chemical Industries Complex, Natref, Omnia Fertilizer, Karbochem, Safripol and Sigma Colliery. The Wonderwater strip-mining operation represents a further source of fugitive dust emissions, but has not been quantified yet (VTPA AQMP Baseline Report, 2007).

The location of the Sasolburg sampling site for July 2006 and March 2007 was at 26°49'12.00"S latitude and 27°51'9.81"E longitude. The site was situated in a field between various industries (Figure 3.6). This site can be classified as an industrial

site and consequently industrial activities are suspected to be the main contributor of atmospheric particulate matter at this site.

Figure 3.6: *The Sasolburg site: MiniVol samplers are on the roof of sampling station.*

3.2.4. Meteorological data of the sampling campaigns

The meteorological data for July 2006 and March 2007 (Table 3.1) were of the Sasolburg site. This was the only site equipped to measure meteorological conditions and was assumed to represent the meteorological conditions of the Vanderbijlpark and Vereeniging sites as well.

Table 3.1: Meteorological conditions of the winter (July 2006) and summer (March 2007) aerosol campaigns conducted in the Vaal Triangle.

Monitoring campaign	Avg wind direction	Avg wind speed	Average Temp	Avg Relative Humidity	Rainfall
Winter 2006	300°	3.1-5.1 m/s	10°C (0.24-22°C)	43%	0-10 mm
Summer 2007	220°	5.1-8.2 m/s	22°C (9.9-32.02°C)	28%	25-50 mm

The average wind speed and direction were obtained from wind roses from the study done by Kleynhans, 2008 as well as the average temperature and relative humidity. The rainfall measurements were based on the preliminary data obtained from the website of the South African Weather Service www.weathersa.co.za.

Thus according to the data in Table 3.1, the atmospheric stability of the Vaal Triangle can be classified as stable during winter and unstable during summer. This is due to lower wind speed as well as the occurrence of stable layers in the morning caused by the low temperatures. Stable conditions lead to increased concentrations of pollutants, especially in the vicinity of the sources resulting in possible higher concentrations in the winter season. Furthermore, the higher rainfall during the summer could have led to pollutants being washed out of the atmosphere.

3.3. SAMPLING

Aerosol samples were collected on pre-fired 47 mm fiber quartz filters. The filters were baked at 500°C for three hours in an oven to remove organic contaminants before use. The sterilized filters were weighed before hand with a microbalance and then put in Petri dishes. Two size fractions of atmospheric particulate matter (fine fraction $PM_{2.5}$ and coarse fraction PM_{10}) were collected with MiniVol Portable Air Samplers (product of Airmetrics). There were two MiniVol samplers per site to obtain PM_{10} and $PM_{2.5}$ samples of each of the three sampling sites. The MiniVol

samplers were set to an airflow rate of 5 litres per minute and sampled for a twenty-four hour period per sample giving a total air volume sampled of 7200 litres. The MiniVol were positioned with the intake upward and were situated in an unobstructed area at least 30 cm away from any obstacles to the air flow. Sampling was conducted over a three day period during the winter season of July 2006 and the summer season of March 2007.

The filters were exchanged after each day of sampling on the site, taking care not to damage or spoil the filters for analysis. The filters were always handled with tweezers whilst wearing surgical gloves. After the filters had been collected at the sites and put in the Petri dishes, they were sealed with masking tape, bagged and refrigerated. The samples were taken out of the refrigerator 24 hours before analysis to reach equilibrium at room temperature. Although the filters were weighed again before analyses, the weighing facilities unfortunately were not temperature and humidity controlled, resulting in possible inaccurate weight differences.

3.3.1. MiniVol portable air samplers

The MiniVol Portable Air Sampler is an ambient air sampler for particulate matter and non-reactive gases (Figure 3.7). The patented low flow technology used in the MiniVol was developed jointly by the U.S. Environmental Protection Agency (EPA) and the Lane Regional Air Pollution Authority in an effort to address the need for portable air pollution sampling technology. It is battery operated and lightweight and ideal for sampling at remote sites or areas without power. The MiniVol features a 7-day programmable timer, a constant flow control system, an elapsed time totalizer, rechargeable battery packs, and an all-weather PVC construction. The MiniVol can be configured to sample for just particulate matter, just gases, or both simultaneously (MiniVol Portable Air Sampler Operation Manual).

The MiniVol Portable Air Sampler is basically a pump controlled by a programmable timer which can be set to make up to six "runs" within 24 hours or throughout a week. The sampler is equipped to operate from either AC or DC power sources. In the DC operational mode, the sampler operates from a battery pack, thus making the sampling site independent of line power. In the AC mode the battery pack is

connected to line power and connected to the sampler unit. This configuration charges the battery while using AC power. An Elapsed Time Totalizer linked in parallel with the pump records the total time in hours of pump operation (MiniVol Portable Air Sampler Operation Manual).

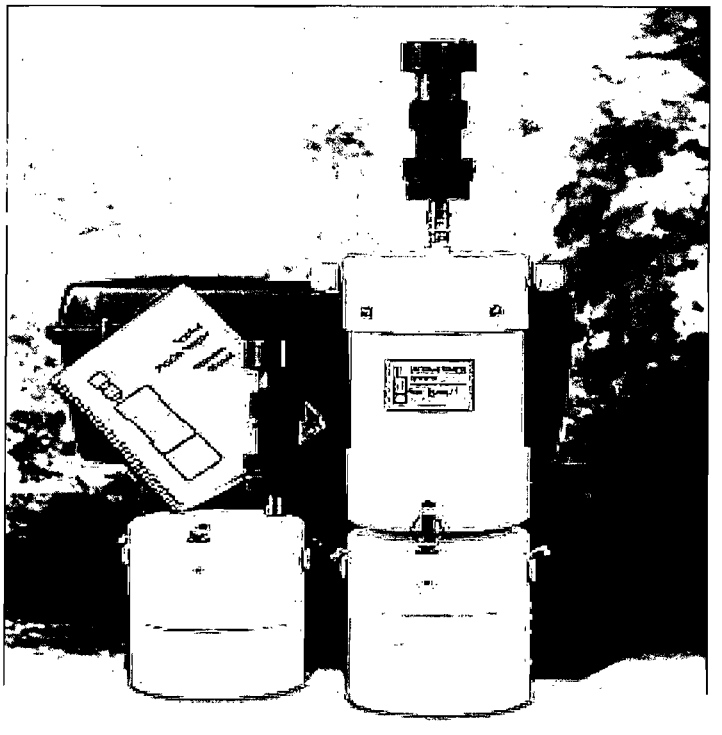


Figure 3.7: *Example of the MiniVol Portable Air Sampler used in this study (MiniVol Portable Air Sampler Operation Manual).*

In the particulate matter (PM) sampling mode, air is drawn through a particle size separator (impactor) and then through a filter medium (Figure 3.8). Particle size separation is achieved by impaction. Critical to the collection of the correct particle size is the correct flow rate through the impactor. For the MiniVol the actual volumetric flow rate must be 5 litres per minute (5 l/min) at ambient conditions. Impactors are available with a 10 micron cut-point (PM_{10}) and a 2.5 micron cut-point ($PM_{2.5}$). Operating the sampler without an impactor allows for collection of total suspended particulate matter (TSP). The inlet tube downstream from the filter takes air to the twin cylinder diaphragm pump. From the pump air is forced through a standard flowmeter where it is exhausted to the atmosphere inside the sampler body (MiniVol Portable Air Sampler Operation Manual).

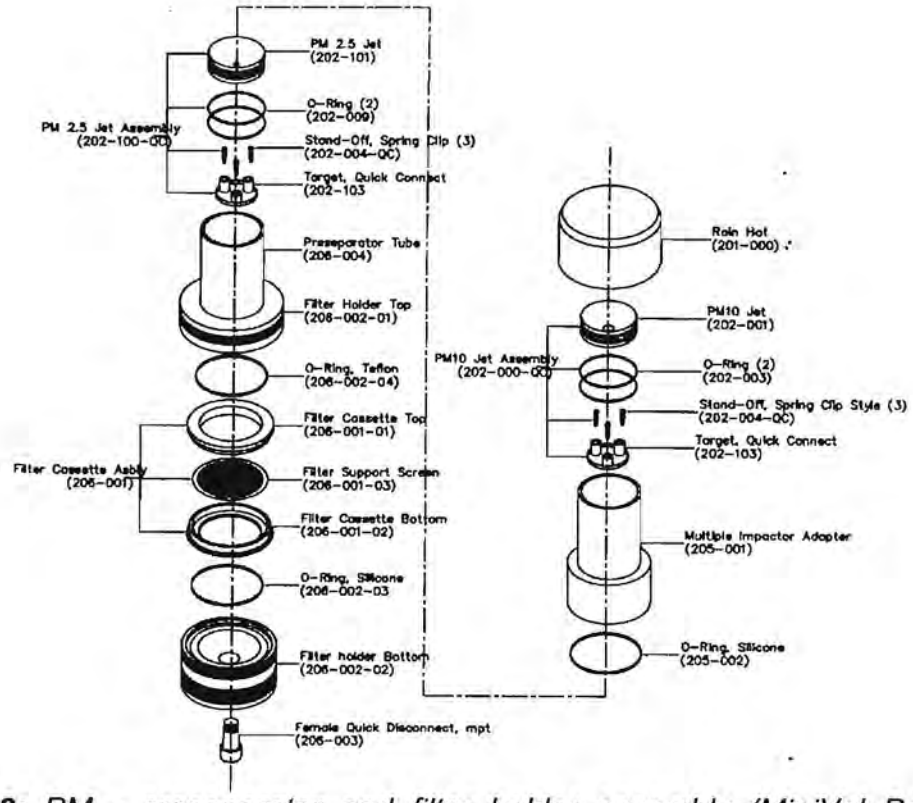


Figure 3.8: *$PM_{2.5}$ preseparator and filter holder assembly (MiniVol Portable Air Sampler Operation Manual).*

The sampling procedures for TSP, PM_{10} and $PM_{2.5}$ are identical except for the configuration of the impactor/filter holder assembly. When sampling for PM_{10} only the PM_{10} impactor is used whereas sampling for $PM_{2.5}$ entails using both the PM_{10} and $PM_{2.5}$ impactor heads linked in conjunction with each other.

Figure 3.9: *$PM_{2.5}$ (left) and PM_{10} (right) impactor setup (MiniVol Portable Air Sampler Operation Manual).*

In this way the air is being drawn first through the PM_{10} impactor and secondly through the $PM_{2.5}$ impactor. For this reason the impactor setup for PM_{10} is smaller than that of $PM_{2.5}$ as can be seen in Figure 3.9 (MiniVol Portable Air Sampler Operation Manual).

3.4. SAMPLE PREPARATION AND ANALYSIS

3.4.1. Gas chromatography analyses of the filter samples

The method that was used for the preparation of aerosol filter samples for GC analysis was adapted from the method of Kawamura and Ikushima (1993). Kawamura and Ikushima collected urban aerosol samples in Tokyo on quartz fiber filters (Pallflex, 20 x 25 cm) by using a high-volume air sampler (Shibata, HVC-1000). The sampling campaign was from the spring of April 1988 to the winter of February 1989. Air was sucked through the filters for 14-52 hours at a flow rate of 1 m^3 min^{-1}. 21 urban aerosol samples were used for the analysis of LMW dicarboxylic acids. The method from Kawamura and Ikushima is as follow:

1. One-fourth of a quartz filter was cut in pieces and extracted under ultrasonication with pure water (10 ml x 3) which was prepared in an all glass apparatus by distillation of Milli-Q water after oxidizing organic impurities with potassium permanganate.
2. The extracts were concentrated down to ca. 1 ml by using a rotary evaporator under a vacuum and then they were passed through a glass column (Pasteur pipette) packed with quartz wool to remove particles such as black carbon and filter debris.
3. The extracts were transferred to a ground glass test tube (10 ml), concentrated by a rotary evaporator under a vacuum and further concentrated to almost dryness under a nitrogen stream.
4. A total of 0.25 ml of 14% BF_3/n-butanol was added to the sample and the test tube was sealed with a glass stopper, Teflon tape and clamp.
5. The acids and reagent were mixed under ultrasonication for 10 s and then heated at 100°C for 30 min to derive dicarboxylic acid dibutyl esters.

6. The esters were extracted with 5 ml of n-hexane after adding 3 ml of pure water and 0.2 ml of acetonitrile, the latter makes the excess butanol transfer into the aqueous phase more effectively.
7. The hexane layer was further washed with pure water (3 ml x 2).
8. The esters were dried by using a rotary evaporator and a nitrogen blow-down system and were then dissolved in 100μL of hexane.
9. The diacid butyl esters were determined with a Hewlett Packard 5890 GC equipped with a split/splitless injector, fused-silica capillary column (UP-2, 0.3mm x 25 m, Hewlett Packard) and an FID detector.
10. Peak areas were calculated with a Hewlett Packard 3396A integrator.
11. Peak identification was performed by a comparison of GC retension times with those of authentic standards.
12. Identification of the esters was confirmed by mass spectral analysis using a Finnigan-MAT ITS-40 GC-MS system

3.4.1.1. Derivatization

Characterization of polar compounds such as dicarboxylic acids by GC-MS requires that they first be derivatized, i.e., converted to less polar compounds, so that they will elute through a GC column (Graham *et al.,* 2002). BF_3 -Butanol, 10% w/w (10% boron trifluoride in butanol) is particularly useful for preparing n-butyl esters for a variety of mono- and dicarboxylic acids, including saturated straight and branched short chain (C_1-C10) fatty acids, 2-hydroxy and 2-keto fatty acids, and simple aromatic acids. Another benefit of derivatization is that it improves peak shapes and reduces adsorption losses. For dicarboxylic acids and many multifunctional carboxylic acids, derivatization is essential for successful GC analysis (Product Specification, Supelco).

Carboxylic acids can be esterified by alcohols in the presence of a suitable acidic catalyst as can be seen in Figure 3.10. The initial step is protonation of the acid to give an oxonium ion (1), which can undergo an exchange reaction with an alcohol to give the intermediate (2), and this in turn can lose a proton to become an ester (3). Each step in the process is reversible but in the presence of a large excess of the alcohol, the equilibrium point of the reaction is shifted so that esterification proceeds

virtually to completion. However, in the presence of water, which is a stronger electron donor than aliphatic alcohols are, formation of the intermediate (2) is not favoured and esterification will not proceed fully (Christie, 1993).

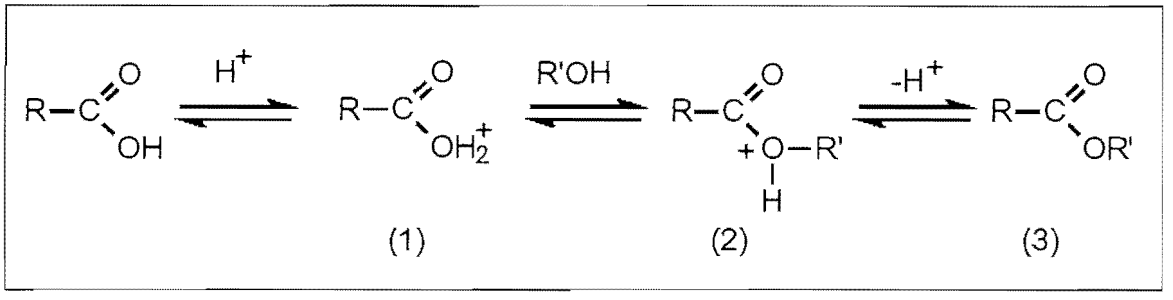


Figure 3.10: *Acid-catalyzed esterification of fatty acids (Christie, 1993).*

Esterification of a carboxylic acid involves heating the carboxylic acid with an acid catalyst in an alcohol solvent, such as BF_3/n-Butanol (Figure 3.11). The catalyst protonates an oxygen atom of the COOH group making the acid much more reactive to nucleophiles. An alcohol molecule ($CH_3(CH_2)_3OH$) then combines with the protonated acid, to yield the ester product (R-COO-$(CH_2)_3CH_3$) with loss of water. Esterification is a reversible reaction and water must be removed to drive the reaction to the right and obtain a high ester yield (BF_3 Butanol, 10% w/w, Product Specification, Supelco).

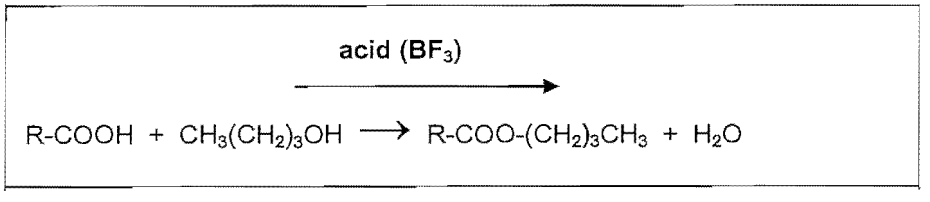


Figure 3.11: *Esterification reaction with BF_3/n-Butanol (BF_3 Butanol, 10% w/w, Product Specification, Supelco).*

3.4.1.2. Laboratory equipment

- Quartz fiber 47 mm filters, G.I.C. Scientific cc.
- Tweezers
- Non-Sterile latex examination gloves, Medtex
- UV reactor

- 40 ml glass beaker
- Graduated 10ml pipette
- Macro pipette controller, Aldrich
- Parafilm, Aldrich
- Ultrasonic bath
- VV 2000 Rotary evaporator system, Heidolph.
- Vacuum pump
- Vacuum grease
- Quickfit expansion adapter, Top NS joint 29/32 and Bottom NS joint 14/23, Aldrich
- Keck Joint Clips (29/32 and 14/23), Aldrich
- Quickfit round bottom flasks (50 ml NS joint 14/23), Aldrich
- Quickfit pear shaped flasks (10 ml NS joint 14/32), Aldrich
- Cork flask support ring, I.D. x O.D. 30 mm x 80 mm, Aldrich
- Glass column (Pasteur pipette)
- Quartz wool, Separations
- Nitrogen blow-down system
- Glass stoppers
- Heating Plate, FALC Instruments
- Aluminum heating block
- Micro-Reaction vessel (3 ml), Supelco
- Push-button valve screw cap, Aldrich
- Spinvane magnetic stirring bar (for 3-5 ml vials), Aldrich
- Sample-Lok series A-2 gas syringe (1 ml), Aldrich
- Sample-Lok series A-2 syringe needles, Aldrich
- Suba-Seal silicone rubber septa (fits neck I.D. 14.0mm), Aldrich
- Economy Blue Septa Sheet 11.5", CRS (Separations)
- Brand Silberband burette (10 ml) with straight stopcock, Aldrich
- Brand Blaubrand micro burette (5 ml) Bang pattern with lateral stopcock, Aldrich
- Hirschmann Ringcaps Micro Capillary Pipette (100 □l pipette, length 125mm), Aldrich
- Micro pipette controller, Aldrich
- Crimp Neck Vials, 2 ml, Separations

- 11 mm Crimp Top seal, polypropylene septum, Separations
- Hand-operated aluminium cap crimper, O.D. 8 mm, Aldrich

3.4.1.3. Laboratory chemicals

- Milli-Q water system (18 $M\Omega cm^{-1}$)
- BF_3/n-butanol, puriss., ~ 10% (~1.3M), Fluka
- Hexane, purum ≥98.0% (GC), Fluka
- Acetonitrile, ACS reagent, ≥ 99.5%, Aldrich
- Nitrogen cylinder (UHP)
- Oxalic acid, puriss. p.a., anhydrous, ≥ 99% (RT), Fluka
- Malonic acid, purum,≥ 98.0% (T), Fluka
- Succinate acid, puriss. p.a., ACS reagent, 99.5% (T), Fluka
- Glutaric acid, assay 99%, Aldrich
- Adipic acid, puriss. p.a., ≥ 99.5% (HPLC), Aldrich
- Pimelic acid, purum, ≥ 99.0% (GC), Fluka
- Suberic acid, assay 98%, Aldrich
- Azelaic acid, puriss., ≥ 99.0% (GC), Fluka
- Sebacic acid, assay 99%, Aldrich
- Phthalic acid, puriss. p.a., ≥ 99.5% (T), Fluka
- Maleic acid, puriss., ≥99.0% (HPLC), Fluka
- Fumaric acid, assay 99%, Aldrich

3.4.1.4. Gas chromatography-mass spectroscopy

Chromatography is the separation of a mixture of compounds (solutes) into separate components so that they can be identified and quantified. By separating the sample into individual components, it is easier to identify (qualitative) and measure the amount (quantitative) of the various sample components. There are numerous chromatographic techniques and corresponding instruments; Gas chromatography (GC) is one of these techniques. In gas chromatography (GC), a moving gas (the mobile phase) carries the sample across a stationary phase (the solid support found within a GC column). To be suitable for GC analysis, a compound must have

sufficient volatility and thermal stability. GC is normally used when the sample can be vaporized below 400-450 °C. A powerful and widely used combination is to couple a GC to a mass spectrometer (MS) to form a GC-MS system (http://www.gmi-inc.com).

In the normal mode of operation, a sample consisting of a mixture of organic compounds which are volatile at a temperature of 275 °C is introduced to the head of the column with a syringe. Helium serves as a carrier gas to move the sample through the column. During passage through the column (a fused silica capillary with a wall coating of a thermally stable, non-volatile liquid), the mixture is separated into individual components. As each component elutes from the column, it is introduced to the MS where a mass spectrum for each species is obtained and stored in a computer. The spectrum is interpreted, either manually or by a computer search, to identify the compounds (http://www.gmi-inc.com). In this study an Agilent 6890 GC with 5973 MSD as detector was used in separating and identifying the dicarboxylic acids. Compounds were identified with the MS database (NIST).

3.4.1.4.1. Gas chromatography

Every gas chromatograph (Figure 3.12) includes the following key components: flow controller, a sample introduction device, column, oven, detectors, and data handling system. In gas chromatography (GC), the sample is vaporized and injected onto the head of a chromatographic column. Elution is brought about by the flow of an inert gaseous mobile phase. In contrast to most other types of chromatography, the mobile phase does not interact with molecules of the analyte; its only function is to transport the analyte through the column. Carrier gases include helium, argon and nitrogen which are chemically inert. Gas-liquid chromatography, which is usually shortened to gas chromatography, is based upon the partition of the analyte between a gaseous mobile phase and a liquid phase immobilized on the surface of an inert solid through adsorption or by chemical bonding (Skoog *et al.,* 1997).

Gas chromatographic separation occurs because of differences in the positions of adsorption equilibria between the gaseous components of the sample and the stationary phases. In GC the distribution ratio is dependent on the component vapor

pressure, the thermodynamic properties of the bulk component band and affinity for the stationary phase (http://www.gmi-inc.com).

The most common of gas chromatographic detectors is the flame ionization detector (FID). This detector produces an electrical signal that varies with the amount of analyte exiting the chromatographic column (Skoog *et al.*, 1997). Another GC detector that is very powerful is the mass spectrometer (MS). When coupled to a GC the detection system itself is often referred to as the mass selective detector or more simply the mass detector. Placed at the end of a chromatographic column in a manner similar to the other GC detectors, the mass detector is more complicated than the FID because of the mass spectrometer's complex requirements for the process of creation, separation, and detection of gas phase ions. A capillary column is most often used in the chromatograph because the entire MS process must be carried out at very low pressures (~10^{-5} torr) and in order to meet this requirement a vacuum is maintained via constant pumping using a vacuum pump.

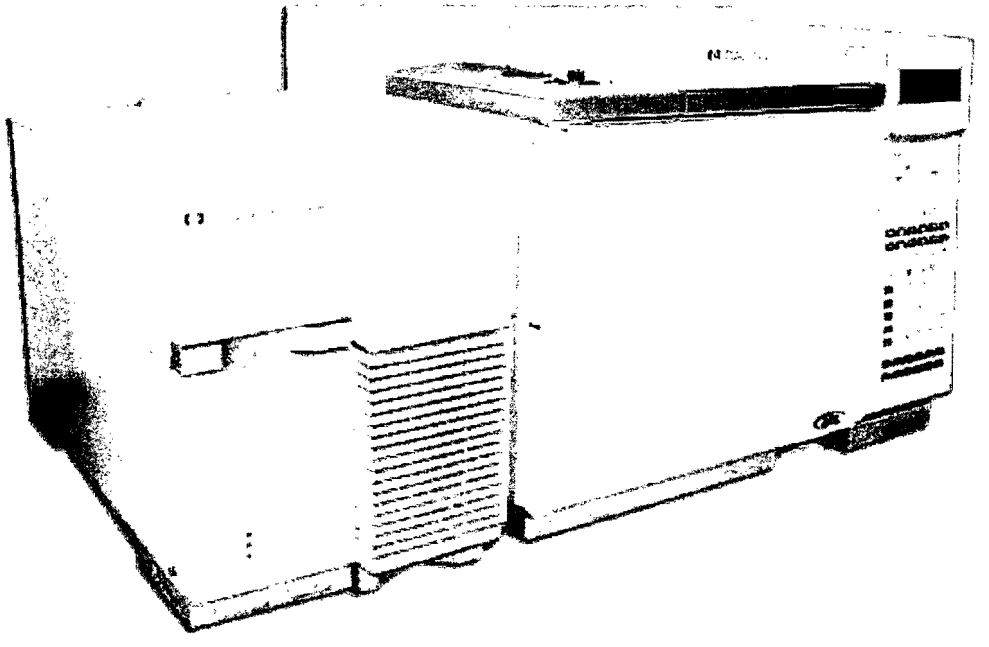


Figure 3.12: *Agilent 6890 GC with a 5973 MSD as detector (http://www.gmi-inc.com)*

The high costs of the pump, ionization source, mass filter or separator, ion detector, and computer instrumentation and software has limited the wide application of the

MS detector system as compared to the less expensive FID GC detector. However, the power of this technique lies in the production of mass spectra for each of the analytes detected instead of merely an electronic signal that varies with the amount of analyte. These data can be used to determine the identity as well as the quantity of unknown chromatographic components with an assuredness simply unavailable by other techniques (http://www.gmi-inc.com).

3.4.1.4.2. Mass spectroscopy

In mass spectroscopy the sample is converted to gas-phase ions. With an energetic atomization source a substantial fraction of the atoms produced are ionized, usually as singly charged positive ions. The ions of different atomic masses are then separated in a device called a mass analyzer to produce the mass spectrum. The separation is on the basis of the mass-to-charge ratio of the ionic species. Thus in general a mass spectrometer consists of an ionization source, a mass-selective analyzer, and an ion detector. Since mass spectrometers create and manipulate gas-phase ions, they operate in a high-vacuum system (Skoog *et al.,* 2004).

The general operation of a mass spectrometer is to:

- Create gas-phase ions.
- Separate the ions in space or time based on their mass-to-charge ratio.
- Measure the quantity of ions of each mass-to-charge ratio.

A quadrupole mass filter consists of four parallel metal rods arranged as can be seen in Figure 3.13. Two opposite rods have an applied potential of (U+Vcos(wt)) and the other two rods have a potential of -(U+Vcos(wt)), where U is a dc voltage and Vcos(wt) is an ac voltage. The applied voltages affect the trajectory of ions travelling down the flight path centred between the four rods. For given dc and ac voltages, only ions of a certain mass-to-charge ratio pass through the quadrupole filter and all other ions are thrown out of their original path. A mass spectrum is obtained by monitoring the ions passing through the quadrupole filter as the voltages on the rods are varied. There are two methods: varying w and holding U and V constant, or varying U and V (U/V) fixed for a constant w (http://www.gmi-inc.com).

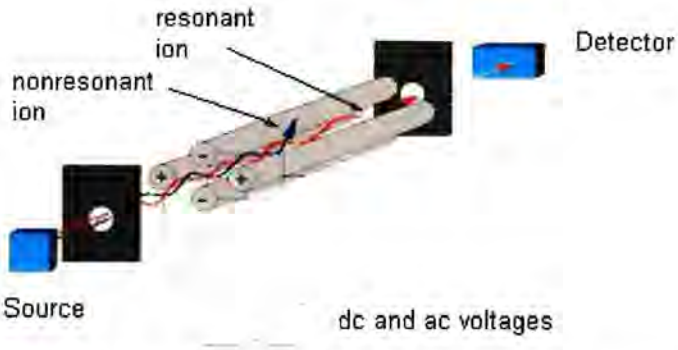


Figure 3.12: *Quadrupole Mass Detector (http://www.gmi-inc.com).*

Quadrupole mass spectrometers consist of an ion source, ion optics to accelerate and focus the ions through an aperture into the quadrupole filter, the quadrupole filter itself with control voltage supplies, an exit aperture, an ion detector, detection electronics, and a high-vacuum system (http://www.gmi-inc.com). Mass spectrometers use the difference in mass-to-charge ratio (m/e) of ionized atoms or molecules to separate them from each other. Mass spectrometry is therefore useful for quantification of atoms or molecules and also for determining chemical and structural information about molecules. Molecules have distinctive fragmentation patterns that provide structural information to identify structural components.

3.5. ION CHROMATOGRAPHY ANALYSIS OF THE FILTERS

Preparation of the quartz filter samples for IC analysis was adapted from the method of Khare *et al.* (1998). Khare *et al.*, analyzed for formate and acetate (monocarboxylic acids) on collected PM_{20} aerosol samples in Dayalbagh India for the winter of 1994 (December and February, N=20) and for the summer of 1995 (May and June, N=17). Their aerosol samples were collected on PTFE filters of 1.2 μm pore size by use of a single-stage open-face 47 mm diameter filter holder at a flow rate of 15 (±) liters per minute for 24 hours. The filters were extracted 2 to 3 days after sampling. The samples were injected into the IC without dilution. Samples were spiked with known concentrations of organic acids to confirm the presence of formate and acetate. All concentrations were calculated based upon the peak heights of the standard that were prepared daily from a 100 ppm stock solution. The extraction procedure was as follow:

1. The filter was wetted with 0.5 ml methanol and 5 ml deionised water was added. This was shaken using a mechanical shaker for 15 minutes.
2. Deionised water (10 ml) was again added and the sample shaken for another 15 minute period. Polyethylene bottles were used in the extraction process as well as for storing the samples in.
3. To test for complete extraction, filters which had been extracted in the above manner were again subjected to the same procedure; the levels of both formate and acetate were below detection limits in these samples.

Although the above method was used only for the quantification of monocarboxylic acids, formate and acetate on TPFE filters, it was expected that this method could also be used to quantify dicarboxylic acids. Analysis of the quartz filter samples was performed by the ICS-3000 Reagent-Free Ion Chromatography (RFIC) system from Dionex.

3.5.1. Laboratory equipment and chemicals

- Milli-Q water (18 $M\Omega cm^{-1}$)
- Methanol, LC-MS CHROMASOLV for HPLC, ≥99.9%, Fluka
- Glass funnel
- Watch glass
- Micro balance
- Volumetric flasks (1 l)
- Volumetric flask (500 ml)
- Tweezers
- Graduated 1 ml pipette
- Graduated 5 ml pipette
- Graduated 10 ml pipette
- Graduated 25 ml pipette
- Macro pipette controller, Aldrich

3.5.2. Ion chromatography specifications

Ion chromatography is a form of liquid chromatography where retention is predominantly controlled by ionic interactions between the ions of the solute and counter ions that are situated in, or on, the stationary phase. For example, to separate organic acids, it is the negatively charged acid ions that need to be selectively retained. It follows that the stationary phase must contain immobilized positively charged cations as counter ions to interact with the acid ions to retain them. Conversely, to separate cations, the stationary phase must contain immobilized anions as counter ions with which the cations can interact. Ion exchange stationary phases are available in mainly two forms. One form (probably the most popular) consists of cross-linked polystyrene polymer beads of an appropriate size which has been suitably treated to link ionic groups to the surface. The other form is obtained by chemically bonding ionic groups to silica gel by a process similar to that used to produce bonded phases. These materials are called ion exchange media, a term which has given rise to the term ion exchange chromatography as an alternative to ion chromatography. Ionic substances can also be adsorbed on the surface of a reverse phase media and act as an adsorbed ion exchanger. The mobile phase is made to contain a small percentage of a soluble organic ionic material (e.g. tetrabutyl ammonium dihydrogen phosphate or n-octyl sulphonate). These substances are adsorbed onto the surface by dispersive interactions between the alkyl groups of the agent and those of the bonded phase and act as counterions. In general ion chromatography is one of the more difficult types of liquid chromatography to exploit and is most often used for analysis of anions for which there are no other rapid analytical methods (http://www.chromatography-online.org/topics/ion/chromatography.html).

The IC used in this study was the ICS-3000 Reagent-Free Ion Chromatography (RFIC) system from Dionex (Figure 3.13). The system was provided by Astrochem Consultants (PTY) Ltd. It consists of an Autosampler (AS), Eluent Generator (EG), Dual Pump (DP) and a Detector/Chromatography (DC) Module. The ICS-3000 is an IC with integrated chromatography software called Chromeleon. The ICS-3000 has three electrolytic technologies which is eluent generation, impurity trapping and suppression (ICS-3000 RFIC System Brochure). The column used in this study was the IonPac AS18 (2 x 250 mm) Analytical Column in combination with the IonPac

AG18 Guard Column. The packing specifications of the columns can be seen in Table 3.2 (IonPac AS18 Product Manual).

Several types of EluGen cartridges are available for use with the EG Module. Each cartridge contains 900 ml of the appropriate electrolyte concentrate solution for eluent generation. The EGC II KOH EluGen Cartridge generates potassium hydroxide eluent for anion exchange separations and was used in this study (ICS-3000 Ion Chromatography System Operator's Manual).

An IonPac AG18 Guard Column is normally used with the IonPac AS18 Analytical Column. A guard is placed prior to the analytical column to prevent sample contaminants from eluting onto the analytical column. It is easier to clean or replace a guard column than it is an analytical column. Replacing the AG18 Guard Column at the first sign of peak efficiency loss or decreased retension time will prolong the life of the AS18 Analytical column (IonPac AS18 Product Manual).

Table 3.2: Stationary phase of the AS18 (2 x 250 mm) guard and analytical columns (IonPac As18 Product Manual; Dionex Corporation, 2005).

Columns	Particle Diameter µm	Substrate X-linking %	Latex Diameter nm	Latex X-linking %	Column Capacity µeq/column[b]	Functional Group
AS18 2 x 250 mm	7.5	55	65	0[a]	75	Alkanol quaternary ammonium
AG18 2 x 250 mm	13	55	65	0[a]	2.5	Alkanol quaternary ammonium

[a] The effective X-Linking after functionalization is 8%.

[b] **Analytical Column resin composition:** supermacroporous polyvinylbenzyl ammonium polymer cross-linked with divinylbenzene.
Guard Column resin composition: microporous polyvinylbenzyl ammonium polymer cross-linked with dininylbenzene.

The function of the AS Module is to deliver samples to the system. The AS Module also protects samples from contamination by its metal-free flow path and chemically inert vials. The AS chamber furthermore has a solid-state cooling function that preserves heat-sensitive samples. The SP/DP Dual Pump Module offers two

complete pumping systems in one module to operate simultaneously or separately. If only one chromatography system is run the second high-performance dual-piston pump can be used for preconcentrating samples or to deliver post-column reagents. The ICS-3000 pump module has a pump made of chemically inert materials and has built-in dynamic mixers which ensure that only homogeneous blends reach the column. The ICS-3000 pump's exclusive piston seal wash system regularly rinses the parts of the pistons and seals that are exposed to air. This prevents abrasive salt crystals from being left by evaporation of eluent solutions or buffers, greatly extending piston seal life. The system also monitors the amount of eluent that seeps past the piston seals, notifying when the seepage rate indicates that seals are due for replacement (ICS-3000 RFIC System Brochure).

The EG Module generates high-purity eluents for single or dual systems by using only deionised water. It supports dual-component eluents such as carbonate/bicarbonate and gradient-compatible eluents such as KOH, NaOH and MSA. The EG automatically transforms deionised water into high-quality eluent at

Figure 3.13: *ICS-3000 Reagent-Free Ion Chromatography system (ICS-3000 RFIC System Brochure).*

the exact concentration needed for the separation run. This eliminates the variability that occurs with manually prepared eluents. The DC is a high-performance environmental chamber that precisely controls temperatures of valves, columns suppressors and detectors. Functions of the DC module includes maintaining extremely stable temperatures for optimum IC performance; providing convenient access to all flow paths while minimizing dead volumes; supporting single-system and dual-system configurations; offering revolutionary electrochemical detection capabilities and also simplifying complex applications with optional Automation Manager (AM). Precise temperature control eliminates drift and minimizes noise, significantly improving detection sensitivity and stability of response (ICS-3000 RFIC System Brochure).

CHAPTER 4
RESULTS

This chapter contains three sections. The first discusses the qualitative results obtained by the GC. The second section contains the IC simulated separations and method development which is used in the third section for the analysis of the field samples.

4.1. GAS CHROMATOGRAPHY RESULTS

In Chapter 3 the literature method for preparing the aerosol filters for GC analysis was described (Paragraph 3.4). The method from Kawamura and Ikushima (1993) was first tested on a Vanderbijlpark PM_{10} filter from the winter sampling campaign of July 2006. The PM_{10} filter was selected because it also contains the $PM_{2.5}$ fraction which could possibly contribute to higher dicarboxylic acid concentrations for detection. No blank filters were analyzed as background since the pre-combusted blank quart filters got contaminated during the sampling campaign.

This first filter was used to asses the process of extraction, synthesis and the technique of concentrating down to 100μL. With this it became apparent that the equipment could prove problematic in handling volumes of 1mL and 100μL. The sample was completely evaporated by the rotary evaporator into the end flask and could not be used due to possible contamination.

A further 10 filter samples of PM_{10} and $PM_{2.5}$ from Vanderbijlpark, Sasolburg and Vereeniging were extracted individually. However, of the 10 filters only one was semi-successfully analyzed by the GC-MS and was the Vanderbijlpark PM_{10} filter

sampled on the second day of the July 2006 campaign (Figure 4.1 and Table 4.1). The other nine filter extracts were either evaporated by the rotary evaporator, evaporated through the rubber septa of the 2ml GC vials even when refrigerated and wrapped in Parafilm or still contained water in the final stage.

When the final extract (100μl) still contained water, analysis was difficult because the small concentrations of dicarboxylic acids (ng/m^3) could either be in the organic layer (hexane) or in the water phase, or both. Such a sample was sent to the CSIR (Council for Scientific and Industrial Research) for Two Dimensional Gas Chromatograph Time-Of-Flight Mass Spectrometer (GCxGC-TOFMS) analysis but the results did not show any dicarboxylic acid butyl esters (Figure 4.2 and Table 2.2).

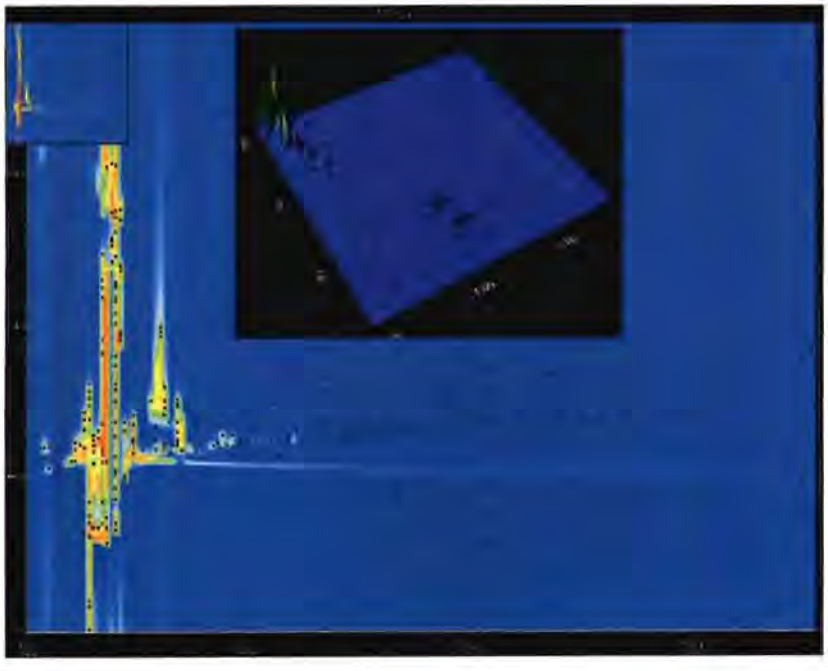


Figure 4.2: PM10 filter extract analyzed by Two Dimensional GCxGC-TOFMS.

Table 4.2: PM_{10} filter analysis by GCxGC-TOFMS.

Peak	Compound	Retention seconds	Similarity
1	Cyclobutylamine	192 , 1.610	825
2	Butane, 1-nitro-	192 , 1.740	740
3	Acetone	196 , 1.140	798
4	Methane, isocyano-	196 , 1.210	954
5	Pentane	200 , 1.070	951
6	Acetonitrile	200 , 1.210	908
7	Butane, 2,2-dimethyl-	208 , 1.070	941
8	Hexane, 2,2-dimethyl-	208 , 1.210	832
9	Pentane, 2-methyl-	220 , 1.120	968
10	1-Hexene, 4-methyl-	224 , 1.120	777
11	Hexane	224 , 1.200	830
12	Nonane, 5-methylene-	224 , 1.240	762
13	Propane, 1-bromo-2-methyl-	228 , 1.230	808
14	Butane, 2-methyl-	232 , 1.210	740
15	1,3-Butadiyne, 1,4-difluoro-	232 , 1.330	871
16	Hexane	232 , 1.400	891
17	1-Butanol, 2-methyl-, (S)-	232 , 1.440	818
18	Pentane, 3-methyl-	232 , 3.670	871
19	Pentane, 2,3-dimethyl-	232 , 3.730	793
20	2-Propenenitrile, 2-chloro-	232 , 3.860	524
21	Acetic acid, dichloro-, ethyl ester	232 , 3.890	495
22	Pentane, 3-ethyl-2,2-dimethyl-	236 , 0.020	813
23	m-Dioxane, 4,5,5-trimethyl-	236 , 0.170	714
24	1-Propyne, 3-chloro-	236 , 0.210	630
25	Pentane, 3-ethyl-2,2-dimethyl-	236 , 0.630	783
26	3-Aza-5-hexylene-1-ol, N,N-dimethyl-,carbaminate ester, bromide	236 , 0.720	675
27	1,4-Dioxane-2,6-dione	236 , 0.760	654
28	1-Buten-3-yne, 1-chloro-, (Z)-	236 , 0.850	590
29	Pentaborane(11)	236 , 1.400	543
30	3-Pentanone	236 , 1.490	731
31	1-Butanol	236 , 1.540	778
32	Pentane, 2,4-dimethyl-	236 , 1.580	806
125	Cyclobutane, 2-ethyl-1-methyl-3-propyl-	312 , 1.220	700
126	1-Propene, 3-(1,1-dimethylethoxy)-	316 , 1.220	642
127	Propylene Carbonate	316 , 1.240	745
128	Pentane, 2,2,4-trimethyl-	316 , 1.260	816
129	Pentane, 2,2,4-trimethyl-	316 , 1.310	770
130	Propane, 1-bromo-2-methyl-	316 , 1.380	784
131	2-Butanone, 3,3-dimethyl-	316 , 1.480	736
132	Propane, 2-nitro-	316 , 1.500	768
133	Azetidine	316 , 1.530	912
134	Azetidine	320 , 1.190	928
135	Pentane, 2,2,4-trimethyl-	332 , 1.180	966
136	3-Pentanol	332 , 1.370	609
137	Hexane, 2,2-dimethyl-	348 , 1.220	950
138	Cyclopentane, 1,1,3-trimethyl-	352 , 1.240	845
139	Cyclohexane, methyl-	356 , 1.290	957
140	Hexane, 2,4-dimethyl-	360 , 1.230	940
141	Cyclopentane, ethyl-	364 , 1.290	927
142	Hexane, 2,2-dimethyl-	368 , 1.160	945
143	Hexane, 3,3-dimethyl-	372 , 1.230	889
144	Cyclopentane, 1,2,4-trimethyl-, (1à,2á,4à)-	372 , 1.250	880
145	1-Butanol, 2-methyl-, (S)-	372 , 1.430	958
146	Pentane, 3-ethyl-	380 , 1.250	912
147	Norbornane	388 , 1.360	931
148	Pentane, 3-ethyl-2-methyl-	392 , 1.260	904
149	Heptane, 2-methyl-	400 , 1.250	943
150	Toluene	404 , 1.500	950
151	Hexane, 2,2-dimethyl-	408 , 1.150	906
152	Heptane, 3-methyl-	408 , 1.260	946
153	Cyclohexane, 1,1,3-trimethyl-	416 , 1.260	764
154	Cyclopentane, 1,2,4-trimethyl-, (1à,2à,4á)-	416 , 1.290	873
155	Benzene, 1,2,4,5-tetramethyl-	416 , 1.700	904
156	1,3-Dimethylcyclohexane,c&t	424 , 1.310	948

Peak	Compound	Retention seconds	Similarity
33	3,8-Cyclodecadiene-1,6-dione, (Z,Z)-	236 , 1.630	512
34	Oxirane, ethenyl-	240 , 0.680	638
35	1,3-Dioxol-2-one	240 , 1.100	625
36	Lidocaine	240 , 1.180	744
37	Butane, 2-methyl-	240 , 1.220	808
38	Propane, 1-(ethenyloxy)-2-methyl-	240 , 1.260	874
39	2,6,10-Dodecatrienal,3,7,11-trimethyl-, (E,E)-	240 , 1.290	595
40	Imidazol, 4-fluoro-	244 , 0.680	739
41	Hexane	244 , 1.270	891
42	Cyclobutane, 1,2,3,4-tetramethyl-	244 , 1.320	738
43	Hexane	244 , 3.780	949
44	Ethane, isocyanato-	248 , 0.710	767
45	Ethanesulfonyl chloride	248 , 0.850	529
46	1,3-Butadiyne, 1,4-difluoro-	248 , 1.110	735
47	2-Propanone, methyl-hydrazone	248 , 1.170	707
48	Hexane	248 , 1.200	886
49	Butane, 2-methyl-	248 , 1.370	791
50	Borinic acid, diethyl-, methyl ester	248 , 1.830	645
51	Decahydroazulen-4-one, 1,1-ethylenedioxy-	248 , 1.920	753
52	Hexane	248 , 2.190	829
53	5-Nonylamine	248 , 2.250	699
54	Methylsulfidtiole	248 , 2.300	503
55	Azetidine	248 , 2.480	815
56	(S)-(+)-4-Isopropyl-2-oxazolidinone	252 , 0.580	750
57	2-Butanone, 3-methyl-	252 , 0.680	732
58	Propanal, 2-methyl-2-(methylsulfonyl)-, oxime	252 , 0.750	692
59	Pentaborane(11)	252 , 1.110	543
60	1-Butanol, 2-methyl-, (S)-	252 , 3.050	779
61	1-Pentanamine	256 , 2.420	573
62	Hexane	256 , 2.530	866
63	2,5-Furandione, dihydro-	256 , 2.560	812
64	1-Hexene, 2,5-dimethyl-	256 , 2.580	835
65	1,3-Dioxol-2-one	256 , 2.750	728
66	Manganese, penta-carbonylmethyl-	256 , 3.070	794

Peak	Compound	Retention seconds	Similarity
157	Hexane, 2,2,3-trimethyl-	432 , 1.260	921
158	Cyclopentane, 1-ethyl-3-methyl-, trans-	436 , 1.310	918
159	Heptane, 2,4-dimethyl-	448 , 1.270	907
160	3-Penten-2-one, 4-methyl-	448 , 1.580	907
161	1à,2á,3à,4á-Tetramethylcyclopentane	452 , 1.280	906
162	Cyclohexane, 1,2-dimethyl-	452 , 1.330	962
163	Benzene, 1,2,4,5-tetramethyl-	452 , 1.380	884
164	Heptane, 3,3-dimethyl-	456 , 1.280	875
165	Cyclohexane, 1,4-dimethyl-, cis-	460 , 1.350	948
166	2(3H)-Furanone, dihydro-3-methyl-	464 , 1.250	848
167	Hexane, 2,3,5-trimethyl-	468 , 1.280	929
168	2,2-Dimethyl-3-heptene trans	468 , 1.300	845
169	Cyclopentane, (1-methylethyl)-	468 , 1.350	884
170	Acetic acid, butyl ester	468 , 1.510	878
171	Heptane, 2,4-dimethyl-	476 , 1.280	917
172	1-Butanol	480 , 1.240	898
173	Cyclopentane, 1-ethyl-2-methyl-, cis-	484 , 1.360	916
174	Heptane, 2,6-dimethyl-	488 , 1.280	938
175	2,2-Dimethyl-1-oxa-2-silacyclo-3,5-hexadiene	496 , 1.330	743
176	Heptane, 3,5-dimethyl-	500 , 1.290	932
177	Cyclohexane, 1,3,5-trimethyl-	500 , 1.330	886
178	Cyclohexane, 1,2-dimethyl-, cis-	500 , 1.390	896
179	Cyclohexane, ethyl-	504 , 1.390	940
180	Cyclohexane, 1,2,4-trimethyl-	516 , 1.340	841
181	3-Nonene	524 , 1.340	843
182	Heptane, 2,3-dimethyl-	532 , 1.310	895
183	Cyclohexane, 1,2,4-trimethyl-, (1à,2á,4á)-	536 , 1.350	916
184	Octane, 4-methyl-	544 , 1.310	941
185	Ethylbenzene	544 , 1.640	960
186	Cyclopentane, 1-methyl-3-(1-methylethyl)-	552 , 1.360	877
187	Octane, 3-methyl-	556 , 1.320	936
188	Pentalene, octahydro-	560 , 1.500	904
189	4-Heptanone	560 , 1.600	877
190	Benzene, 1,3-dimethyl-	560 , 1.630	954

Peak	Compound	Retention seconds	Similarity
67	Propanoic acid,anhydride	260 , 0.670	808
68	Hexane	260 , 0.710	741
69	Propane, 1-(ethenyloxy)-2-methyl-	260 , 0.870	811
70	2-Propen-1-ol, 2-methyl-	260 , 0.940	699
71	Benzenemethanol, à-[1-(ethylmethylamino)ethyl]-	260 , 1.030	850
72	Imidazol, 4-fluoro-	260 , 1.050	706
73	Phenethylamine, à-methyl-N-propyl-	260 , 1.150	637
74	2-Butanone, 3-methyl-	260 , 1.280	804
75	2-Pentanone	260 , 1.380	777
76	2-Propenal	260 , 1.520	602
77	1-Propanamine, 2-methyl-N-(2-methylpropyl)-	260 , 1.590	702
78	Hexane, 2,2,5-trimethyl-	260 , 1.630	681
79	Hexane, 2,2,3-trimethyl-	260 , 1.750	806
80	Pentane, 3-ethyl-2,2-dimethyl-	260 , 1.810	765
81	Pentane, 3-ethyl-2,2-dimethyl-	260 , 2.020	761
82	Decahydroazulen-4-one, 1,1-ethylenedioxy-	260 , 2.090	782
83	Pentane, 2,3-dimethyl-	260 , 2.170	770
84	3-Heptanone, 4-methyl-	260 , 2.190	714
85	Ethanamine, N,N-diethyl-2-[2-(2-methoxyethoxy) ethoxy]-	260 , 2.250	773
86	1-Propanamine, 2-methyl-N-(2-methylpropyl)-	260 , 2.270	721
87	1,2-Ethanediamine, N,N,N',N'-tetraethyl-	260 , 2.290	749
88	2-Butanone, 3-methyl-	260 , 2.460	701
89	2-Imidazolidinone	260 , 2.620	710
90	2H-Tetrazole, 2-methyl-	260 , 2.720	809
91	3,4-Dimethyldihydrofuran-2,5-dione	260 , 2.760	782
92	Benzenemethanol, à-[1-(ethylmethylamino)ethyl]-	260 , 3.060	651
93	Oxetane, 3,3-dimethyl-	264 , 1.920	712
94	3,4-Dimethyldihydrofuran-2,5-dione	264 , 1.950	865
95	Propane, 1-nitro-	264 , 1.970	729
96	Pentane, 3-methyl-	264 , 2.370	876
97	Isobutane	264 , 2.400	757
98	Pentaborane(11)	264 , 2.700	591
99	Isobutyl nitrite	264 , 2.770	755

Peak	Compound	Retention seconds	Similarity
191	Cyclohexane, 1,2,4-trimethyl-	572 , 1.390	911
192	n-Butyl ether	576 , 1.420	973
193	Cyclohexane, 1,2,4-trimethyl-	580 , 1.400	915
194	Cyclopentane, 1-methyl-2-propyl-	584 , 1.380	882
195	cis-1-Ethyl-3-methyl-cyclohexane	592 , 1.400	939
196	4-Heptanol	592 , 1.550	882
197	1H-Indene, 2,3-dihydro-5-methyl-	596 , 0.570	883
198	Benzene, 1,2-dimethyl-	596 , 1.710	890
199	Cyclohexane, 1-ethyl-4-methyl-, cis-	600 , 1.390	925
200	Nonane	604 , 1.330	958
201	3-Ethyl-4-octene	608 , 1.360	794
202	2,3-Butanediol, 2,3-dimethyl-	612 , 3.670	687
203	Cyclohexane, 1-ethyl-4-methyl-, cis-	624 , 1.430	917
204	Indan, 1-methyl-	648 , 0.360	905
205	Octane, 2,5-dimethyl-	648 , 1.330	889
206	Cyclohexane, (1-methylethyl)-	648 , 1.450	885
207	Pentalene, octahydro-2-methyl-	648 , 1.490	839
208	Benzene, (1-methylethyl)-	652 , 1.690	962
209	Decane, 2,6,8-trimethyl-	656 , 1.340	847
210	Cyclohexane, 1,1,2,3-tetramethyl-	660 , 1.400	824
211	Benzene, 1,2,3,5-tetramethyl-	660 , 3.920	880
212	Octane, 2,6-dimethyl-	664 , 1.340	938
213	Cyclohexane, propyl-	664 , 1.450	895
214	Cyclohexane, 1-ethyl-2-methyl-	664 , 1.470	879
215	Heptane, 3-ethyl-2-methyl-	676 , 1.360	868
216	Cyclohexane, 1-ethyl-1,3-dimethyl-, trans-	680 , 1.400	864
217	Octane, 4-ethyl-	700 , 1.360	882
218	Cyclohexane, 1-ethyl-2-propyl-	700 , 1.420	774
219	Hexanal, 2-ethyl-	704 , 1.650	934
220	Benzene, propyl-	704 , 1.750	970
221	Decane, 5-methyl-	712 , 1.360	877
222	3,4-Diethyl-2-hexene	716 , 1.440	844
223	Benzene, 1-ethyl-3-methyl-	716 , 1.790	951

Peak	Compound	Retention seconds	Similarity
100	Pentane, 3-methyl-	268 , 1.000	826
101	2-Pentanone	268 , 1.020	778
102	3-Pentanone, 2-methyl-	268 , 1.320	743
103	3-Buten-2-ol	268 , 1.380	697
104	2-Pentene, 4-methyl-	276 , 1.170	787
105	Pentane, 2-chloro-4-methyl-	276 , 1.240	750
106	Propane-1,3-diamine, 2-t-butyl-	276 , 1.260	783
107	Oxirane, ethenyl-	276 , 1.360	735
108	Nonane, 5-methylene-	276 , 1.420	705
109	Cyclopentane, methyl-	284 , 1.190	894
110	1-Butanol	292 , 1.520	945
111	Hexane, 2-methyl-	296 , 1.200	952
112	Cyclohexane	296 , 1.250	916
113	Benzene	296 , 1.350	824
114	1-Butanol	300 , 1.940	859
115	2-Propenal	300 , 1.970	911
116	1-Butanol	300 , 2.000	766
117	Hexane, 3-methyl-	304 , 1.200	966
118	1-Isopropenyl-3,3-dimethyl-5-(3-methyl-1-oxo-2-butenyl)-cyclopentane	304 , 1.230	655
119	2-Propenal	304 , 1.430	768
120	1-Butanol	304 , 1.470	873
121	1-Butanol	304 , 1.520	879
122	2-Propenal	304 , 1.610	786
123	Cyclopentane, methyl-	308 , 1.170	922
124	1-Butanol	308 , 1.380	954

Peak	Compound	Retention seconds	Similarity
224	Nonane, 2-methyl-	720 , 1.350	879
225	Benzene, 1-ethyl-4-methyl-	724 , 1.760	964
226	Nonane, 3-methyl-	732 , 1.360	939
227	Benzene, 1,2,3-trimethyl-	732 , 1.730	977
228	Pentalene, octahydro-2,5-dimethyl-	744 , 1.490	810
229	Cyclooctane, ethyl-	748 , 1.460	882
230	Benzene, 1-ethyl-2-methyl-	748 , 1.840	960
231	Cyclohexane, 1-methyl-2-propyl-	760 , 1.440	900
232	Cyclohexane, 1-methyl-4-(1-methylethyl)-, trans-	768 , 1.440	853
233	1H-Indene, octahydro-, cis-	776 , 1.630	854
234	Butanoic acid, 1-methylpropyl ester	776 , 1.700	933
235	Benzene, 1,2,3-trimethyl-	780 , 1.820	973
236	Decane	784 , 1.380	940
237	Benzene, (2-methylpropyl)-	804 , 1.740	862
238	Benzene, (1-methylpropyl)-	808 , 1.770	924
239	Benzene, 1-methyl-2-(1-methylethyl)-	824 , 1.800	948
240	Naphthalene	828 , 0.090	940
241	Benzene, 1,2,3-trimethyl-	828 , 1.920	965
242	Benzene, 1-methyl-4-(1-methylethyl)-	832 , 1.790	847
243	Indane	856 , 2.050	945
244	Benzene, 1-ethynyl-4-methyl-	872 , 2.170	912
245	Hexane	880 , 0.990	952
246	Benzene, 1-methyl-3-propyl-	880 , 1.820	971
247	Benzene, 1-methyl-3-propyl-	888 , 1.830	899
248	Benzene, 1-methyl-3-(1-methylethyl)-	888 , 1.860	835

After trying to obtain quantitative analysis with the filter extracts it was decided to obtain commercial available standards to inject directly into the GC-MS for determination of the retension values and separation properties of the dicarboxylic acids. However, only dicarboxylic acids standards and not their dibutyl ester derivates were available. This meant that the standards had to be converted to dibutyl esters via the synthesis process of Kawamura and Ikushima (1993) before it could be injected into the GC.

Twelve dicarboxylic acid standards were purchased as indicated in Paragraph 3.4.1.3. The standards were made up as 1g/L solutions, diluted to ng/m^3 and then used in the synthesis process to produce dibutyl esters. However, the synthesis pathway still could not deliver satisfactory extracts to be analyzed. The next step were then to buy more specialized equipment (glassware, vials, micro pipettes, gas syringes and chemically resistant GC crimp caps) to handle the liquid volumes more effectively. These are also listed with the rest of the equipment in Paragraph 3.4.1.2.

However, before more than a few trial synthesis could be performed it was decided to exchange GC-MS with ion chromatography (IC) as analytical technique. The method by Kawamura and Ikushima (1993) proved to be labour intensive and difficult and could not provide adequate results after one and a half years of continuous effort.

4.1.1. Conclusion and discussion of the one filter extract analyzed by Gas Chromatography - Mass Spectroscopy

Although Kawamura *et al.* (1993, 2005, 2006) conducted several studies using this method and a number of articles were published in peer reviewed journals, it was experimentally found to be very difficult to obtain quantitative and even qualitative results for the WSOC studied using this method. This was due to:

1. The handling intensity required by the method. The expected concentrations of the WSOC were in the ng/m^3 range. Practically the extraction, pre-concentration, synthesis (converting dicarboxylic acids to dibutyl ester derivates) and sample preparation required that each liquid sample had to be transferred 7 times to different mediums (i.e. other solvents or glass containers) before analysis was done on the GC-MS. Considering the extremely low concentrations, such handling intensity is likely to cause losses.

2. The sensitivity of the acid-catalyzed esterification synthesis used to convert dicarboxylic acids to dibutyl esters required that the derivatization reagent BF_3/n-butanol had to be in excess and water to be absent. In the initial step when protonation of the acid took place to produce an oxonium ion (Paragraph 3.4.1), if water (which is a stronger electron donor than aliphatic alcohols) was present, formation of the intermediate was not favoured and esterification would not proceed fully (Christie, 1993). According to Kawamura and Ikushima (1993) the 30 ml water extracted filter sample was to be dried firstly by a rotary evaporator under a vacuum and then with a nitrogen stream. The derivatization agent BF_3/n-butanol was then added to synthesize dibutyl esters; which were then transferred to hexane after 3 ml of water and 0.2 ml acetonitrile were added. The hexane layer was then further washed with 2 aliquots of 3 ml water after which the dibutyl esters were dried by a rotary evaporator and a nitrogen blow-down system. The dried dibutyl esters were lastly dissolved in 100 µl hexane and analyzed with the GC-MS.

This method from Kawamura and Ikushima 1993 is based on the quantitative conversion of the diacids to dibutyl ester derivates. However recovery from the reaction medium may not have been achieved because special precautions had to be taken (Christie, 1993). Short-chain fatty acid esters are volatile and may be lost selectively on refluxing the esterification medium. The fatty acid esters are

more soluble in water than longer chain esters and can be lost in an aqueous extraction step, or they may be distilled off when the extracting solvent is evaporated. Careful removal of excess solvents at low temperatures on a rotary film evaporator is better than using a stream of nitrogen and will keep losses of short-chain esters down, but these cannot be eliminated completely. The best esterification procedures of short-chain fatty acids are those in which heating of the reagents is avoided and in which stages involving aqueous extraction and solvent removal are absent (Christie, 1993).

Further problems encountered with the experimental work were as follow:

- Many efforts were made to remove all the excess water from the extracted filter sample, but there was always water present in the final stages of concentrating the diacids in the hexane layer.
- 2ml GC crimp top vials were used to store the synthesized esters in. The extracted diacids in 100µl hexane could not be stored in the refrigerator for too long due to hexane being so volatile and evaporating through the septa of the crimp top vials. Para film was wrapped around the crimp top of the GC vial in order to stop the evaporation. When this did not lessen the evaporation, other crimp tops with more resistant septa than that of standard rubber were used. This lessened the evaporation effect to an extend, but not completely

- Standard dicarboxylic acids were purchased as standard dibutyl ester solutions are not commercially available. The esterification synthesis of Kawamura and Ikushima (1993) had to be applied to convert the standard dicarboxylic acids to dibutyl esters.

- Special micro equipment had to be bought to contain the small volumes during the synthesis process.

The chromatogram (Figure 4.1) was a single PM_{10} Vanderbijlpark filter sample taken in the winter (July) of 2006. The magnified area contained the dibutyl ester derivates in the 10-27 minute retention time region. Peaks in Figure 4.1 could be divided into three categories according to their functional groups: [1] a first (retention time 6-18 minutes), [2] middle (retention time 20-30 minutes) and [3] last section (retention time 30-46 minutes). Individual peaks were identified with the MS database (NIST) and can be seen in Table 4.1.

The first section mostly contained benzene derivates and cyclic structures. In the middle section dicarboxylic acids, and more specifically, the synthesized dibutyl esters were detected. The last section contained long chain alkane structures. When the extracted WSOC fraction of the filter samples was analyzed for the dibutyl ester derivates, some peaks (C_3, C_4 and C_5 dicarboxylic acids) could be seen but not the expected C_2, which is usually the most abundant diacid. There were also other potential butyl and dibutyl ester peaks (Pentanoic acid, butyl ester, 25.80 minutes and 2-Butenedioic acid(2),dibutyl ester, 22.08 minutes) which were detected. Further more; long chain monocarboxylic acids (C_{16} butyl ester at 30.38 minutes and C_{18} butyl ester at 33.00minutes) were detected in stead of the expected derivatized short chain dicarboxylic acids.

Although the percentage probability of some peaks in Table 4.1 was very low, it was mentioned due to the fact that these peaks in the first and last regions could be seen in Figure 4.1; unlike the lower concentration peaks in the middle section which were enhanced.

Unfortunately only qualitative and not quantitative data of the dibutyl ester derivates and consequently the dicarboxylic acids could be obtained using the GC-MS method. This was due to reasons as discussed in the beginning of this section. Also, the dibutyl esters' concentrations in the middle region were suppressed by the higher concentrations of the first and last retention regions' compounds, which made the peaks difficult to detect and quantify. The

unsatisfactory results using the GC-MS technique necessitated the investigation of other potential analysis techniques for the dicarboxylic acids.

Table 4.1: Identified peaks of the WSOC compounds from the GC-MS chromatogram of Figure 4.1.

Retention (min)	Peak name	Probability (%)
6.48-10.55	Benzene derivates and cyclic alkanes	83-97
10.89	Propanedioic acid, diethyl ester	83
11.89	Benzene 1-ethyl-2,3-dimethyl	91
12.11	Benzene 4-ethyl-1,2-dimethyl	94
13.18	Benzene 1,2,3,5-tetramethyl	91
13.45	Acetaldehyde, N-formyl-N-methyl hydrazane	59
14.80	Naphtalene	91
15.91	Pentanoic acid, 4-oxo, 1-methyl ester	64
17.49	Naphtalene, 2-methyl	90
19.89	Propanedioic acid, dibutyl ester	83
21.60	Butanedioic acid, dibutyl ester	83
22.08	2-Butenedioic acid, dibutyl ester	64
23.20	Pentanedioic acid, dibutyl ester	64
24.49	Decane 2,6,7-trimethyl	36
25.80	Pentanoic acid, butyl ester	50
27.86	1,2-Benzenedicaarboxylic acid, butyl 2-ethylhexyl ester	83
30.38	Hexadecanoic acid, butyl ester	72
33.00	Octadecanoic acid, butyl ester	64
33.26	Octacosane	87
34.30	Heptacosane	90
34.50	Phthalic acid, monocyclohexyl ester	47
35.49	Heptadecane	83
36.88	Pentatriocantane	50
38.52	Eicosane	95
40.50	Octadecane	52

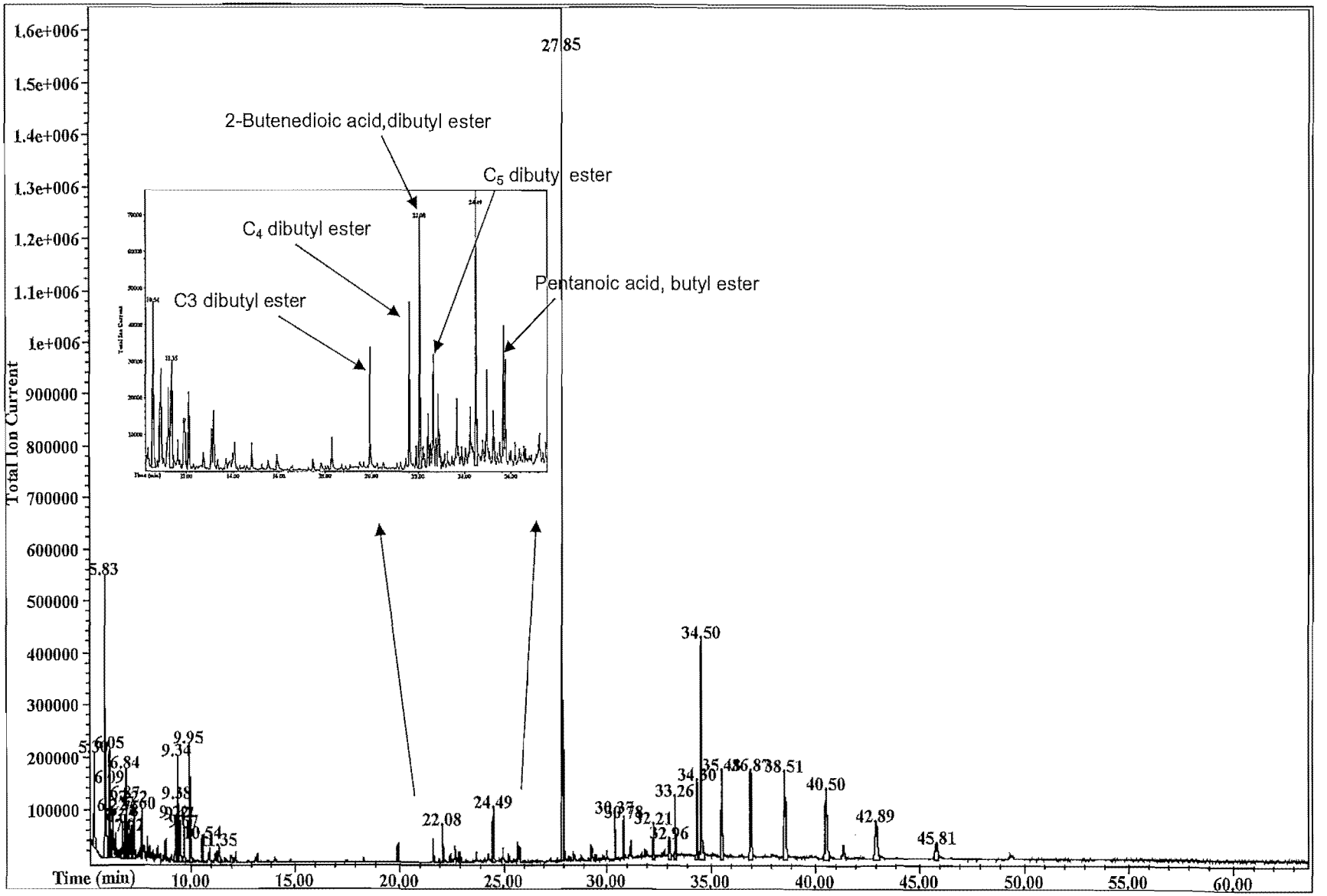


Figure 4.1: GC chromatogram of WSOC extract from an ambient filter.

4.2. ION CHROMATOGRAPHY RESULTS

After the GC-MS methodology failed to deliver satisfactory qualitative and quantitative data, a new technique and methodology had to be investigated. Ion chromatography (IC) was an alternative method that could potentially be used. It is an easier and simpler technique due to the fact that no sample pre-treatment or esterification was needed. The dicarboxylic acid standards could be dissolved in water and injected into the IC without derivatization. The ambient air filter samples could also be extracted with water under ultra sonication and then be injected into the IC (Khare *et al.,* 1998).

The ICS-3000 Reagent-Free Ion Chromatography (RFIC) system from Dionex was used in this study (Paragraph 3.5.2). Additional software called Virtual Column, which is fully integrated into the Chromeleon Chromatography Management System software, was accessed by obtaining a special license (CHROMELEON 6 Virtual Column Brochure). With Virtual Column separation simulator the best column and separation conditions for dicarboxylic acids could be obtained by simulating their behaviour with the software. In this way, optimum conditions could be obtained for the elution of the species before the actual sample was injected into the IC. For this purpose Chapter 4 focuses on Virtual Column and the theoretical simulations of the separation of diacid species and optimal separation conditions. In Chapter 5, the optimum conditions found in Chapter 4 will then be used to analyze the WSOC filter extracts.

4.2.1. Virtual Column

Whether it is a standard IC method or developing a new method, optimizing separations for a study's specific applications are important to deliver better results. Selecting the best column and separation conditions for analysis take valuable time and consume precious samples. With Virtual Column separation

simulator the best column and separation conditions for the study could be determined without wasting valuable field samples. Virtual Column models species' behavior using known retention data and IC-specific retention algorithms. The analytes needing to be separated as well as selecting the Dionex column and eluent system to be modelled only has to be specified. Virtual Column would then display the expected chromatogram together with a resolution map indicating the eluent conditions that will produce the best separations (CHROMELEON 6 Virtual Column Brochure). An example of such a chromatogram can be seen in Figure 4.2.

Virtual Column models all of the most popular Dionex anion-exchange and cation-exchange columns, using hydroxide, carbonate/bicarbonate, and methane sulfonic acid eluent systems. Retention data for hundreds of analytes, obtained from columns carefully selected to be statistically representative of manufacturing lots are already stored in Virtual Column's database. The void time, peak efficiencies and peak asymmetries can be adjusted to more accurately model the performance of the actual columns being used (CHROMELEON 6 Virtual Column Brochure). Thus the first step in method development is selecting a column.

The second step in finding the optimal conditions for a good separation of specific analytes is choosing between isocratic and gradient elution methodology. Column development using a single liquid as the mobile phase is known as isocratic elution. However, to increase the resolving power of the mobile phase it is necessary to change the pH, ionic concentration or polarity continuously. This is known as gradient elution (Wilson and Walker, 2000).

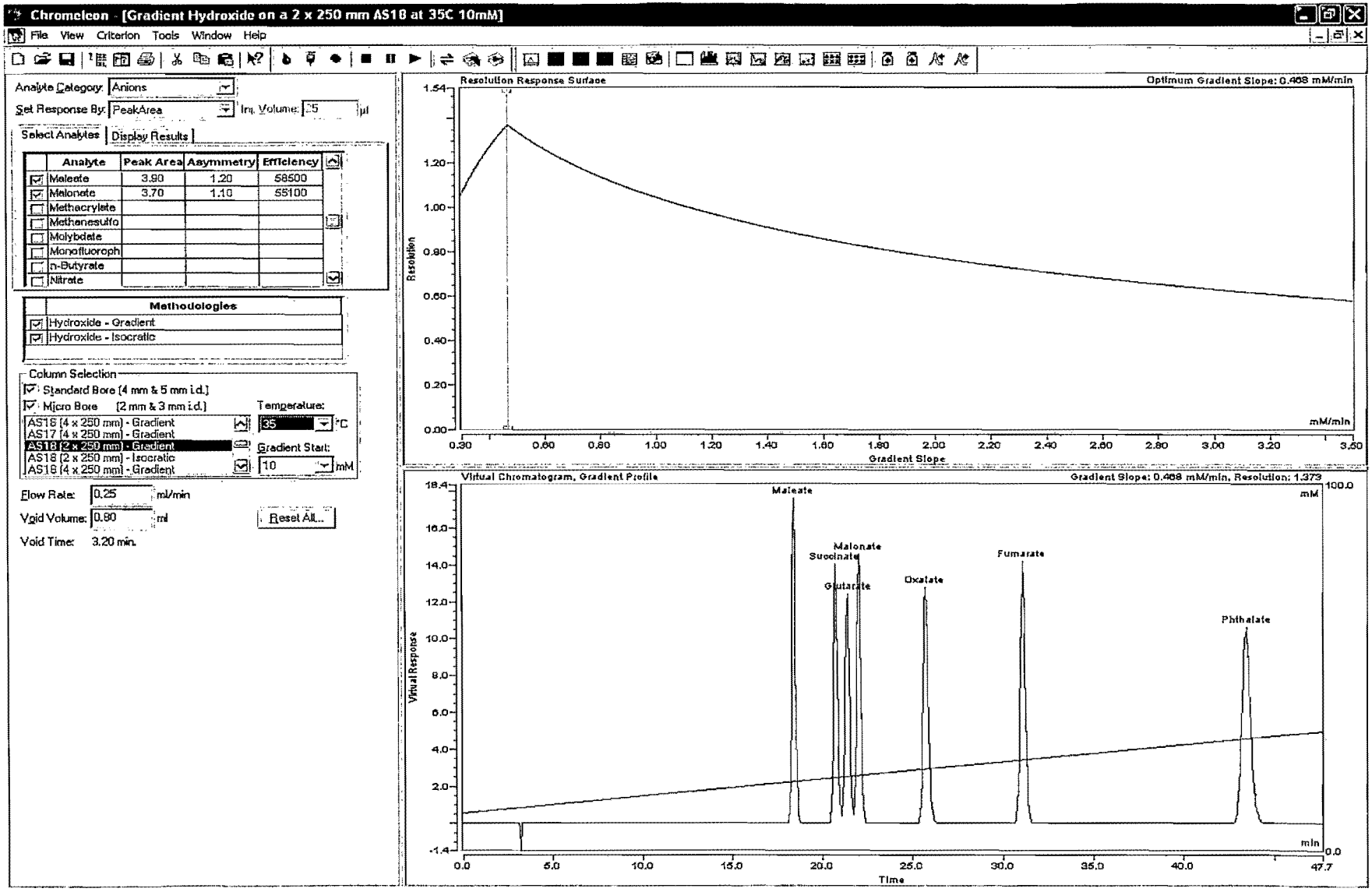


Figure 4.2: *Virtual Column separation simulator task panel and chromatogram.*

The benefit of a concentration gradient is that strongly retained analytes can be eluted faster without compromising the separation of weakly retained analytes. Also, the peak focusing effect of gradient elution makes the analyte peaks taller, sharper, and more symmetric than the peaks of isocratic conditions. Thus, gradient elution can deliver better resolution, higher sensitivity, and lower detection limits than can be achieved with the isocratic methodology. Because gradient elution spread out weakly retained peaks while eluting strongly retained peaks in a reasonable time, challenging samples can be characterized. In a single analysis weakly retained species like fluoride and acetate, moderately retained ions like sulphate and phosphate, and tenacious compounds like perchlorate and polyphosphates can precisely be determined (CHROMELEON 6 Virtual Column Brochure).

In some cases though, gradient methods are not always the best choice. Isocratic methods are sometimes faster, while gradient elution requires time for re-equilibration after each gradient run. With Virtual Column's workflow interface isocratic and gradient methodologies can be compared on the same column, or across a range of columns. In this manner it can be determined whether a gradient or isocratic approach is best for the specific application (CHROMELEON 6 Virtual Column Brochure).

With Virtual Column species' behaviour can closely resemble those of real samples. This can be accomplished by adjusting chromatography parameters such as: void volume, injection volume, analyte peak areas (or approximate concentrations), peak efficiencies and peak asymmetries. With these parameters method robustness can be predicted by modelling flow rate changes, column overloading, or column fouling (CHROMELEON 6 Virtual Column Brochure).

The aim of this chapter was thus to use Virtual Column in finding the best column(s) as well as eluent methodology for the separation of selected

dicarboxylic acids. This was done through a screening process of different columns. The next step was then to adjust certain parameters in finding the optimal separation conditions.

The Virtual Column separation simulator study was divided into 3 sections to:

1. Find the most suitable column through a process of elimination from a list of columns (Paragraph 4.4, Table 4.2);
   - Together with the column screening was the comparison of an isocratic vs. a gradient elution methodology;

2. Determine the optimum temperature at which the diacids would separate the best on the column, and eluent methodology found in step one and

3. to vary the diacid concentration parameters according to literature values and compare the obtained chromatograms with that of Virtual Column's.

All the simulations were done at a constant flow rate of 0.25 ml/min, which is the standard flow rate also used for anion-exchange separation on the ICS-3000 RFIC. It was assumed that the pressure was also constant at ± 1800 psi, though it was not specified on the Virtual Column simulation.

4.2.2. Screening of 7 columns

The dicarboxylic acids found in Virtual Column separation simulator's database were: oxalic (C_2), malonic (C_3), succinic (C_4), glutaric (C_5), phthalic (Ph), maleic (M), fumaric (F) and malic (hC_4). After a few initial test simulations it became apparent that malic acid interfered with C_5 and would be difficult to separate. As mentioned in Chapter 2 (Paragraph 2.6) the expected abundance of dicarboxylic acids according to Ho *et al.* (2006) are firstly C_2 followed by either C_3 or Ph with

the fourth most abundant diacid being C_4. Maleic acid would be the next abundant diacid followed by C_5, malic acid and lastly fumaric acid. Maleic and fumaric acids are cis and *trans* isomers from each other with the *cis* configuration of maleic acid being the predominant dicarboxylic acid. Because malic acid is less abundant than the other dicarboxylic acids and due to its apparent problematic separation with C_5; the acid was not considered further in the screening process or the study. Though C_6 and C_9. are often mentioned in the literature to distinguish between anthropogenic (C_6) and biogenic (C_9) origin of dicarboxylic acids (Paragraph 2.2.3), these diacids were not in the Virtual Column separation simulator's database and were also not used in the screening process or in the rest of the study.

The dicarboxylic acids that were thus used in the screening process were: C_2-C_5, Ph, M and F. The list of columns made available by Virtual Column's database depended on the specified species. There were 9 columns (Table 4.2) to choose from when the above mentioned seven dicarboxylic acids were specified. All the specifications of the columns listed in Table 4.2 were from the IonPac Product Manuals AS11, AS11-HC, AS15, AS16, AS17, AS18, AS19 and AS20.

Several initial test simulations were run and this indicated that columns AS11 (4x250mm, gradient elution) and AS11-HC (4x250mm, gradient and isocratic elution) were not suited for the separation of the dicarboxylic acids. The screening was thus done with the remaining 7 columns (Table 4.2) which included the ICS-3000 RFIC column currently in use (AS18 (2x250mm). The columns' internal diameter (ID) was either 2mm or 4mm. With the exception of column AS18 (2x250mm), all the other columns available in Virtual Column's database were 4mm columns. Initially the column temperature was kept at 23°C for screening purposes, although in some cases the temperature could be changed to 30 and 35°C. The column temperature would later on be varied to

Table 4.2: Columns listed in Virtual Column separation simulator's database for the potential separation of dicarboxylic acids.

Columns	Particle Diameter µm	Substrate X-linking %	Latex Diameter nm	Latex X-linking %	Column Capacity µeq/column[b]	Functional Group	Hydrophobicity
AS11 4 x 250 mm Gradient elution	13	55	85	6	45	Alkanol quaternary ammonium	Very low
Substrate X-linking: Macroporous (2000 A) divinylbenzene/ethylvinylbenzene polymer **Latex X-linking:** Microporous polyvinylbenzylammonium polymer cross-linked with divinylbenzene **Elution:** Hydroxide is normally used for gradient elution							
AS11-HC 4 x 250 mm Isocratic & Gradient elution	9	55	70	6	290	Alkanol quaternary ammonium	Medium-Low
Substrate X-linking: Macroporpous (2000 A) divinylbenzene/ethylbenzene polymer **Latex X-linking:** Microporous divinylbenzene/ethylvinylbenzene polymer **Elution:** Hydroxide for gradient & sodium carbonate/bicarbonate for isocratic elution							
AS15 4 x 250 mm Gradient elution	9	55	na	na	225	Alkanol quaternary ammonium	Medium-High
Column packing: Macroporous (100 A) divinylbenzene/ethylvinylbenzene polymer **Elution:** Any suppressible ionic eluent that does not exceed the capacity of the Anion Self-Regenerating Suppressor can be used							

Columns	Particle Diameter µm	Substrate X-linking %	Latex Diameter nm	Latex X-linking %	Column Capacity µeq/column[b]	Functional Group	Hydrophobicity
AS16 4 x 250 mm Gradient elution	9	55	na	na	170	Alkanol quaternary ammonium	Ultra-low
Column packing: Macroporous (2000 A) divinylbenzene/ethylvinylbenzene polymer **Elution:** Hydroxide eluents can be used							
AS17 4 x 250 mm Gradient elution	10.5	55	na	na	30	Alkanol quaternary ammonium	Low
Resin composition: Microporous polyvinylbenzyl ammonium polymer cross-linked with divinylbenzene **Elution:** Hydroxide dradient elution or any eluent that does nor exceed the capacity of the Anion Self-Regenerating Suppressor can be used							
AS18 2 x 250 mm Isocratic & Gradient elution	7.5	55	65	0 *	75	Alkanol quaternary ammonium	Low
AS18 4 x 250 mm Isocratic & Gradient elution	7.5	55	65	0 *	285	Alkanol quaternary ammonium	Low
* The effective Latex X-linking after functionalization is 8 % **Column resin composition:** Supermacroporous polyvinylbenzyl ammonium polymer cross-linked with divinylbenzene **Elution:** Hydroxide or any suppressible ionic eluents that does not exceed the capacity of the suppressor can be used							

Columns	Particle Diameter µm	Substrate X-linking %	Latex Diameter nm	Latex X-linking %	Column Capacity µeq/column[b]	Functional Group	Hydrophobicity
AS19 4 x 250 mm Isocratic & Gradient elution	7.5	55	na	na	240	Alkanol quaternary ammonium	Low
Resin composition: Supermacroporous polyvinylbenzyl ammonium polymer cross-linked with divinylbenzene **Elution:** Hydroxide gradient elution or any suppressible ionic eluent that does not exceed the capacity of the Anion Self-Regenerating Suppressor ULTRA II can be used							
AS20 4 x 250 mm Isocratic elution	7.5	55	na	na	310	Alkanol quaternary ammonium	Low
Resin composition: Supermacroporous polyvinylbenzyl ammonium polymer cross-linked with divinylbenzene **Elution:** Hydroxide isicratic elution							

find the optimum temperature at which the best column from the screening process could perform the separation of the dicarboxylic acids (paragraph 4.5). All the chromatograms of the screening can be seen in Appendix A.

All the columns considered during the screening process were run with the seven specified dicarboxylic acids, first in isocratic mode and then in gradient mode. Each of the columns with the selected diacids was also run a third and fourth time with added inorganic ions: fluoride, chloride, nitrate and sulphate in first isocratic and then in gradient mode. These ambient inorganic ions could possibly be on the sampled aerosol filters and would elute along with the WSOC fraction. In most cases though the inorganic anions eluted first and only in a few instances interfered with the separation of the dicarboxylic acids. An example of the four simulations done with each column is shown in Table 4.3.

Table 4.3: Screening of an ideal and realistic scenario.

Column	Mode	Specifications	Scenario	Temp.
AS18 (4x250mm)	Isocratic	Diacids only	Ideal	23°C
AS18 (4x250mm)	Gradient	Diacids only	Ideal	23°C
AS18 (4x250mm)	Isocratic	Diacids and inorganic ions	Realistic	23°C
AS18 (4x250mm)	Gradient	Diacids and inorganic ions	Realistic	23°C

In a few cases however some columns were unable to perform the simulations in both the gradient and isocratic mode and only gave either isocratic or gradient, depending on the capabilities of the columns. In the following section it will be clearly specified each time whether the column was capable of both the elution modes or rather just one.

4.2.2.1. AS18 (2x250mm)

This column was run in both the gradient and isocratic mode, providing four chromatograms (Appendix A, chromatogram A.1-A.4) as seen in Table 4.4. If two or more species, be it either dicarboxylic acid or inorganic anion, are marked with the same colour, it indicates that these peaks were closely linked and were not clearly

separated. If species are colour and encircled, it means these two or more species eluted at the exact same time, resulting in one integrated rather than multiple peaks. An example of this is Figure 4.3 which was the separation chromatogram of the dicarboxylic acids and inorganic anions run in the isocratic mode. C_4 and maleic acid are marked in yellow, showing these two peaks were closely linked resulting in peak overlap. The three peaks (C_3, C_5 and sulphate) marked in green however are encircled and indicate that these peaks eluted at the same time to form one integrated peak instead of three.

Table 4.4: AS18 (2x250mm) at 23°C.

	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S
Isocratic	✓	✓	✓	✓	✓	✓	✓				
Gradient	✓	✓	✓	✓	✓	✓	✓				
Isocratic	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

Out of this first screening, in the ideal scenario where there were no inorganic anions present and the separation was done in the gradient mode, the peaks were sharp due to peak focusing and spaced quite good with no overlap. In the more realistic approach the gradient separation was better than that of isocratic, again due to peak focusing while the isocratic separation had quite broad peaks. The gradient elution was also able to separate C_5 from sulphate and C_3, even if it was only marginally.

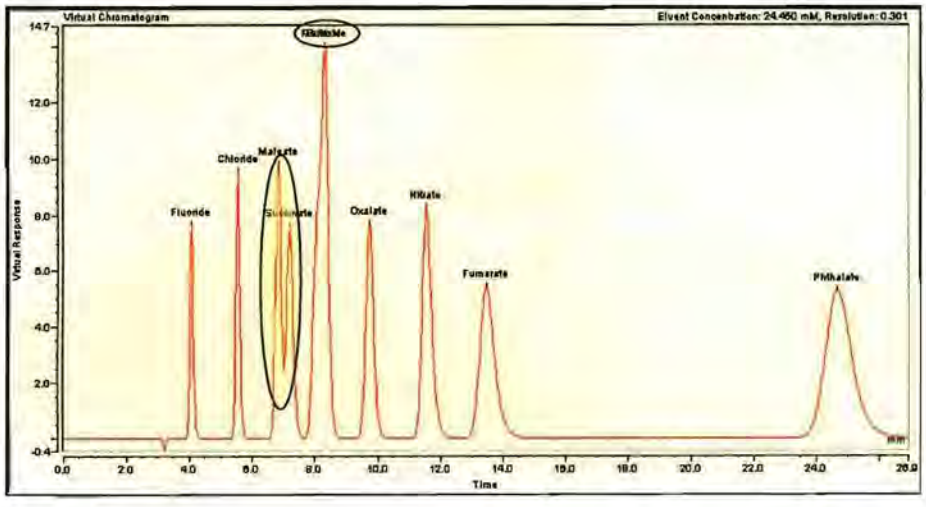


Figure 4.3: *AS18 (2x250mm) in isocratic mode with overlapping peaks.*

4.2.2.2. AS18 (4x250mm)

Table 4.5: AS18 (4x250mm) 23°C.

	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S
Isocratic	✓	✓	✓	✓	✓	✓	✓				
Gradient	✓	✓	✓	✓	✓	✓	✓				
Isocratic	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

This column could operate in both the gradient and isocratic mode (Appendix A, chromatograms A.5-A.8). Good separation of the dicarboxylic acids, either from the ideal or realistic point of view however could not be achieved, as can be seen from Table 4.5. There was peak overlap with C_3 and C_4 in the ideal scenario, isocratic mode. Gradient elution was marginally better with peak focusing and slight separation of C_3 and C_4 to give two peaks instead of one, as was the case with the isocratic elution. The dotted circle of C_3 and C_4 in the gradient elution indicates that these species are closely linked with the two peaks still visible as apposed to a solid line which indicates that the species eluted as a single peak.

With the isocratic realistic scenario the separation was poor with broad peaks and six species being closely linked from which four species overlapped to give two separate individual peaks, as can be seen in Figure 4.4. This is indicated with the blue circle marking C_3 and C_4 and the black circle of nitrate and sulphate. The gradient elution was marginally better with peak focusing but still having the problem of the closely linked C_3, C_4, C_5 and sulphate (Figure 4.5).

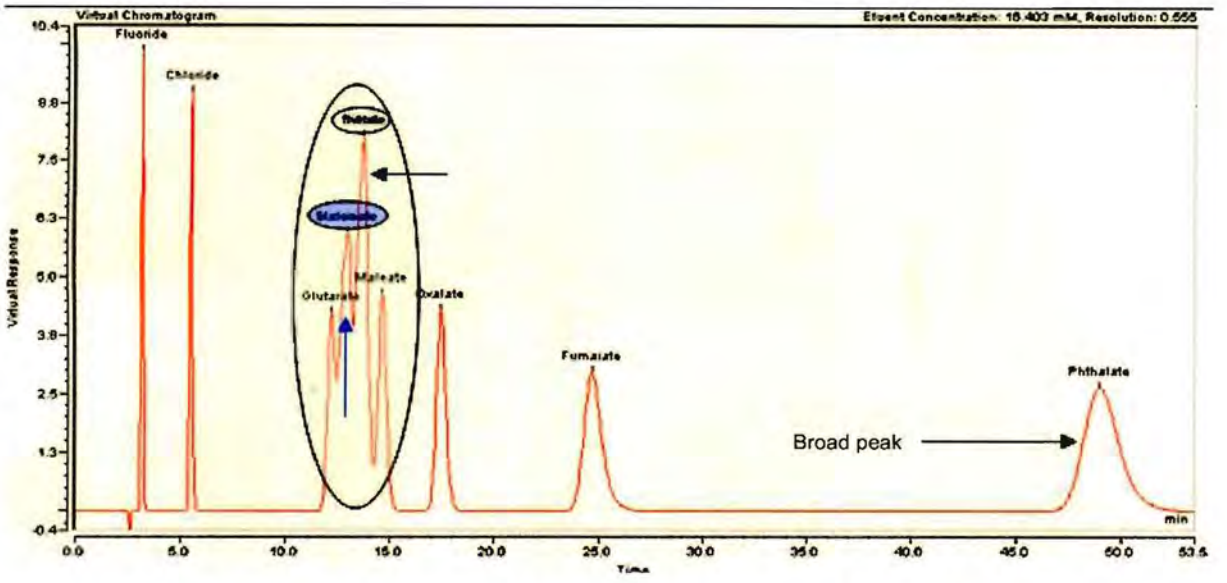


Figure 4.4: *AS18 (4x250mm) in isocratic mode of the ideal scenario.*

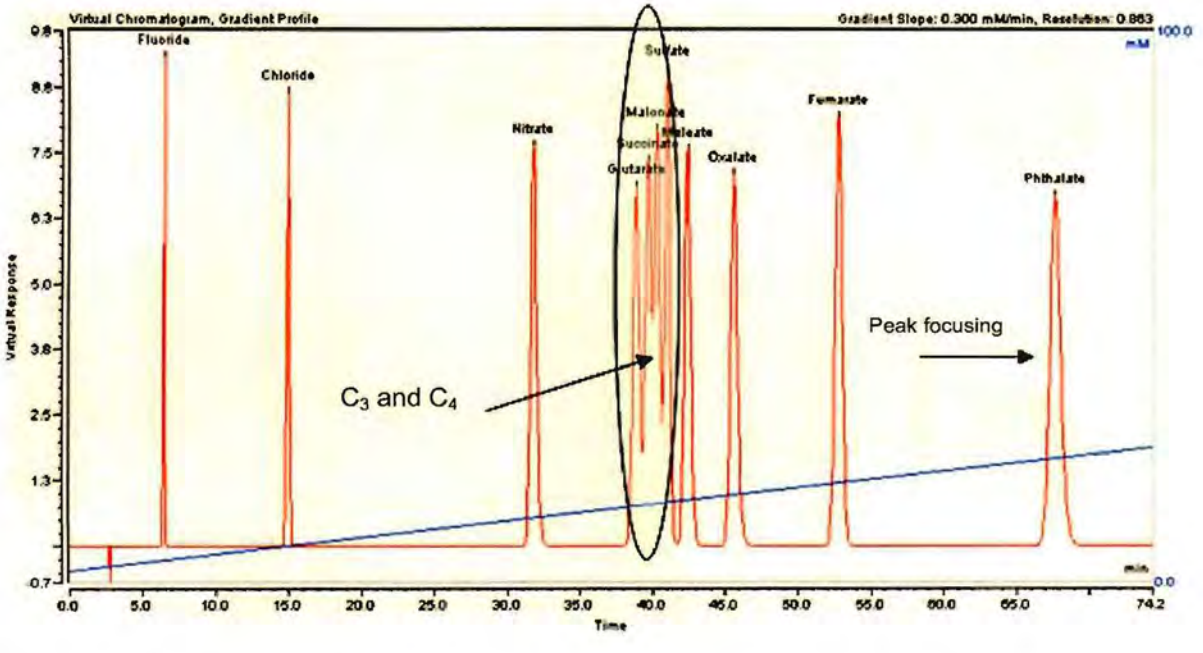


Figure 4.5: *AS18 (4x250mm) in gradient mode of the realistic scenario.*

4.2.2.3. AS19 (4x250mm)

Table 4.6: AS19 (4x250mm) 23°C.

	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S
Isocratic	✓	✓	✓	✓	✓	✓	✓				
Gradient	✓	✓	✓	✓	✓	✓	✓				
Isocratic	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

This column could operate in both the gradient and isocratic mode as demonstrated in Table 4.6. In this instance good separation could not be achieved (Appendix A, chromatograms A.9-A.12). Looking at the ideal scenario, there was a problem with the separation of C_2-C_5 as well as with maleic acid. With this column the isocratic separation was marginally better than that of the gradient elution. Isocratic elution gave broad peaks whereas gradient elution gave sharper peaks, but which unfortunately led to the diacids being more closely linked than was the case with isocratic elution. This can be seen by the dotted encircling of C_4, C_5 and M in the isocratic mode and the solid encircling in the case of the gradient elution. The realistic scenario's isocratic and gradient elutions were not any better.

4.2.2.4. AS20 (4x250mm)

Table 4.7: AS20 (4x250mm) 23°C.

	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S
Isocratic	✓	✓	✓	✓	✓	✓	✓				
Isocratic	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

In this instance the column could only perform isocratic separations and not that of gradient elution (Table 4.7). As seen in the previous instances; gradient elution was the better choice of the two eluent methodologies and in this case did not prove any

different. In the ideal scenario the peaks were broad with 5 species (C_2, C_3, C_4, C_5 and M) contributing to peak integration and overlapping in two instances (Appendix A, A.13 and A.14). In the realistic approach the anions contributed to the poor separation by nitrate and phthalic acid being closely linked. as was the case in previous instances. Further indications that this column was not suitable were evident in that the anions (sulphate and chloride) also could not be separated from each other as was the case in previous instances.

4.2.2.5. AS15 (4x250mm)

Table 4.8: AS15 (4x250mm) 23°C.

	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S
Gradient	✓	✓	✓	✓	✓	✓	✓				
Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

In this instance the column could only separate the dicarboxylic acids in the gradient mode (Table 4.8). This was the first column which separation compared well to the AS18 (2x250mm) and current ICS-3000 RFIC column. In this simulation though, the ideal scenario was still plagued by peak integration of C_4 and C_5 as well as peak overlap by C_3, whereas that was not the case with the AS18 (2x250mm) column. In the realistic scenario the situation was the same as that of the ideal scenario, only maleic acid and sulphate were now contributing to peak overlap. The realistic scenario of column AS18 (2x250mm) also had closely linked C_3, C_4, C_5 and sulphate (Appendix A, chromatogram A.4) but to a lesser extend than was the case with this column (Appendix A, chromatogram A.15 and A.16).

4.2.2.6. AS16 (4x250mm)

Table 4.9: AS16 (4x250mm) 23°C.

	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S
Gradient	✓	✓	✓	✓	✓	✓	✓				
Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

This column could only separate the diacids and inorganic anions via gradient elution (Table 4.9). In the ideal scenario separation was poor with peak overlap as well as integration with all the diacids except Ph (Appendix A, chromatograms A.17 and A.18). The realistic scenario was exactly the same with sulphate now also being linked with maleic acid to form one integrated peak. This column thus was not a good candidate for the separation of dicarboxylic acids.

4.2.2.7. AS17 (4x250mm)

Table 4.10: AS17 (4x250mm) 23°C.

	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S
Gradient	✓	✓	✓	✓	✓	✓	✓				
Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

This column was also only able to separate the dicarboxylic acids via gradient elution (Table 4.10). This column was the second column to compare competently with the AS18 (2x250mm) column. Both the ideal and realistic scenario showed the same results with the anions making no difference. The peaks were sharp and well defined and the only faulty points were C_4 andC_5 as well as C_2 and fumaric acid contributing to two peak overlapping (Appendix A, chromatograms A.19 and A.20).

4.2.2.8. Conclusion of column and elution screening

There were 3 columns that showed promising chromatograms. To summarize; the three columns with their separation patterns as well as elution methodologies can be seen in Table 4.11.

Table 4.11: Best 3 columns to separate dicarboxylic acids.

Column	Eluent	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S
AS18 (2x250mm)	Gradient	✓	✓	✓	✓	✓	✓					
	Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
AS15 (4x250mm)	Gradient	✓	✓	✓	✓	✓	✓	✓				
	Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
AS17 (4x250mm)	Gradient	✓	✓	✓	✓	✓	✓	✓				
	Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

With column AS18 (2x250mm) the ideal scenario was perfect. The realistic scenario had marginal overlap of C_4 and M as well as peak overlap of C_5 with the integrated peak of C_3 and sulphate (Appendix A, chromatograms A.2 and A.4). However, $BaCl_2$ can be used to remove sulphates from the WSOC sample before injection into the IC (private correspondence with Donald Vinnecombe, Astrochem Consultants (PTY) Ltd), making C_3 elute as a single sharp peak. Gradient elution provided good peak focusing in both instances. The most abundant diacid, C_2 eluted as a single sharp peak, which is very good. The fact that C_5 is closely linked with C_3 is unfortunate, but because C_5 is the second least abundant diacid of the selected 7 diacids of the screening procedure, this overlap is negligible when choosing a suitable column.

In column AS15 (4x250mm) the ideal scenario was not so good with peak integration of C_4 and C_5, as well as trailing by C_3. The realistic scenario could have been considered if the integrated peak was of sulphate and a diacid because then the sample could have been treated with $BaCl_2$ to obtain a single sharp diacid peak. As it is, C_4 and C_5 could not be separated, leading to this column being discarded as a potential choice.

With column AS17 (4x250mm) the ideal scenario was not as good as column AS 18's, but still provided a good separation with no peak integration and only marginal peak overlap. A good aspect about this column is that the realistic scenario looked exactly the same as that of the ideal scenario; the anions did not influence the diacids' separation at all. The only problem was that one of the overlapping peaks was of oxalic acid with fumaric acid. Oxalic acid is the diacid that according to literature is usually the most abundant diacid, thus the preference should be to elute oxalic acid as a single, sharp peak rather than overlapped with a species.

Thus concluded, the best column for the separation of the dicarboxylic acids was between column AS17 and AS18 (2x250mm). Column AS18 (2x250mm) was finally chosen on grounds that this column eluted C_2 as a single sharp peak, and column AS17 could not, as well as the possibility of being able to separate C_3 from sulphate by adding BaCl to the solution before hand.

4.2.3. Temperature optimization of column AS18 (2X250mm)

The second step was to find the optimal temperature for column AS18 (2x250mm) at which to perform the separation of dicarboxylic acids at. As expected out of the screening process with the columns, the gradient elution proved the better methodology in separating the diacids. The focus of the optimum temperature screening was thus on gradient, rather than isocratic elution. Isocratic elution was also done though, but only to reaffirm that the isocratic separation was still not as good as the gradient elution, even if the temperature was varied.

Also, the ideal scenario was already optimized in the column screening step (with gradient peak focusing and no peak overlaps, Appendix A, chromatogram A.2), leading to the temperature only being optimized for the realistic scenario (Appendix A, chromatogram A.4). The ideal scenario is still represented in the tables though because the temperature influences the duration of the separation, as can be seen in the retention columns. All the chromatograms of the temperature optimization screening (in isocratic and gradient elution of the ideal and realistic scenario), can be seen in Appendix B.

The following tables are of the realistic scenario of column AS18 (2x250mm) at the three different temperatures of the Virtual Column separation simulator. The temperature options were: 23 °C, 30 °C and 35°C.

4.2.3.1. Temperature: 23°C

Table 4.12: AS18 (2x250mm) at 23°C.

	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S	Retention (min)
Gradient	✓	✓	✓	✓	✓	✓	✓					**52. 30**
Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	**16.30**

Ideal & Realistic			**Ideal**	**Realistic**
Flow rate:	0.25ml/min	**Gradient slope:**	0.300mM/min	3.500mM/min
Void volume:	0.80ml	**Gradient start:**	10mM	10mM
Void time:	3.20min	**Resolution:**	1.522	0.223

The chromatograms in Table 4.12 were already discussed in the screening process (Paragraph 4.2.2.1, Chromatograms A.1-A.4). The ideal scenario was perfect with no peak overlap or integration. The realistic scenario's problematic areas were C_3 and C_5 as well as C_4 with maleic acid. The only addition to the table is that of the duration of the run. Interesting to note was that the realistic scenario's run time was shorter than that of the ideal situation's. Also the ideal and realistic scenarios' parameters were the same, except for the gradient slope and resolution parameters (Table 4.12).

4.2.3.2. Temperature: 30°C

Table 4.13: AS 18 (2x250mm) at 30°C.

	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S	Retention (min)
Gradient	✓	✓	✓	✓	✓	✓	✓					**56.20**
Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	**56.20**

Ideal & Realistic			**Ideal**	**Realistic**
Flow rate:	0.25ml/min	**Gradient slope:**	0.300mM/min	0.300mM/min
Void volume:	0.80ml	**Gradient start:**	10mM	10mM
Void time:	3.20min	**Resolution:**	1.564	0.388

At this temperature separation seemed to improve (Table 4.13; Appendix B chromatograms B5.-B.8). The problems of peak overlap by C_4 and M as well as the problem of C_5 with C_3 were no longer a factor. Sulphate and C_3 still formed one integrated peak but as previously mentioned, this could be solved by precipitating the SO_4^{2-} with Ba^{2+}. The only difference of this separation from that of the initial 23°C, was that the nitrate and maleate peaks tended to overlap a bit. Maleic acid is the third least abundant diacid of the list according to literature, and was thus not that much reason for concern. The retention time was also much longer than was the case at 23°C. This was due to the resolution increase (0.223 to 0.388 for the realistic and 1.522 to 1.564 for the ideal scenario) which resulted in a better separation. The parameters in Table 4.13 were the same except for the resolution, which was less in the case of the realistic scenario.

4.2.3.3. Temperature: 35°C

Table 4.14: AS18 (2x250mm) at 35°C.

	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S	Retention (min)
Gradient	✓	✓	✓	✓	✓	✓	✓					**47.70**
Gradient	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	**59.10**

Ideal & Realsitic			**Ideal**	**Realistic**
Flow rate:	0.25ml/min	**Gradient slope:**	0.468mM/min	0.300mM/min
Void volume:	0.80ml	**Gradient start:**	10mM	10mM
Void time:	3.20min	**Resolution:**	1.373	0.526

At this temperature the separation still looked good (Table 4.14; Appendix B, chromatograms B.9-B.12). It was only C_4 and C_5 which could prove problematic. They overlapped marginally but except for that the separation looked better than the separation done at 23°C. The run time was also the longest of the three temperatures. The parameters that vary in Table 4.14 were that of the gradient slope and resolution.

4.2.3.4. Conclusion

Table 4.15: AS18 (2x250mm) gradient elution at 23, 30 and 35°C.

	Temp.	C_2	C_3	C_4	C_5	Ph	M	F	Cl	F	N	S
Gradient	**23°C**	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Gradient	**30°C**	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Gradient	**35°C**	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

All three temperature options delivered good separation with gradient peak focusing, but 30°C and 35°C were marginally better (Table 4.15). The optimal temperature was decided as 30°C because maleic acid is less abundant than either C_4 or C_5,

which posed a problem at 35°C. The only real problem at 30°C was the minimal overlap of nitrate with maleic acid. The runtime of 30°C was also a few minutes shorter than the runtime of the realistic scenario run at 35°C.

4.2.4. Diacid concentration optimization

The third step after selecting the best suited column and the optimal temperature of that column was to determine in which way the diacid concentrations could influence the quality of the separation. In the following section Table 4.16 portrays three different diacid concentration scenarios. Six chromatograms of the three different diacid concentrations can be seen in Appendix C.

The first 2 chromatograms (Appendix B, B.6 and B.8) were of column AS18 (2x250mm) at 30°C portraying the ideal and realistic scenario in gradient elution at the optimal Virtual Column concentrations. This was already discussed in the previous section (Paragraph 4.2.3.2). The concentrations of the diacids were automatically provided by the Virtual Column separation simulator on selecting the desired column and species to be separated. The next chromatograms (Appendix C, chromatograms C.3-C.6) were the separation of manually altered diacid concentrations.

The first altered diacid concentration chromatograms were of the ideal and realistic scenarios (Appendix C, C.3 and C.4), representing the lowest concentrations that were obtained in a case study of Ho *et al.* (2006). The second range of altered diacid concentration chromatograms (Appendix C, C.5 and C.6) was of the highest concentrations obtained in the study of Ho *et al.* (2006).

Something that should be kept in mind though is that the analysis of the dicarboxylic acids of 2006 done in Ho et al's. case were analyzed with a GC-MS and not an IC. The concentrations are in some cases very low and although it registers on the IC, Virtual Column separation simulator allowed only 2 decimal numbers in the concentration parameter, showing the values as 0.00 instead of 0.00252 mg/l. The inorganic anions in the realistic case scenario were also manually changed to two orders of magnitude smaller to adapt to the change in diacid concentrations. Table

4.16 contains the converted diacid concentrations of the values obtained in ng/m^3 by Ho *et al.*, (2006). The conversion calculations are in Appendix C.

Table 4.16: Concentration optimization of values from Virtual Column and literature.

	Virtual Column mg/l	Lowest diacid concentrations		Highest diacid concentrations	
		Literature ng/m^3	Conversion mg/l	Literature ng/m^3	Conversion mg/l
C_2	4.10	63.8	0.015312	767	0.18408
C_3	3.70	10.5	0.00252	145	0.0348
C_4	3.70	31.1	0.003144	121	0.02904
C_5	3.60	2.82	0.006768	28.1	0.006744
Ph	5.90	40.1	0.009624	105	0.0252
M	3.90	2.21	0.0005304	37.2	0.008928
F	4.70	0.29	0.0000696	8.66	0.0020784
Cl	1.90		0.01		0.01
Fl	1.00		0.02		0.02
N	3.70		0.03		0.03
S	3.80		0.04		0.04

In the first and second chromatograms where Virtual Column specified the diacid concentrations, the separation was good (Paragraph 4.2.3.2). The only problem was that the concentrations were much higher (easily two and more orders of magnitude higher) than what the literature predicted.

Although the separation of low concentrations (Appendix C, Chromatograms C.3 and C.4) was not as good as that of Virtual Column's, the ideal and realistic separations were still quite good. In the ideal scenario, peak focusing as well as detectable and quantifiable peaks was achieved, making it marginally better than the realistic scenario. The peaks of the diacids in the realistic scenario were suppressed by the higher concentration inorganic anions; and this contributed to the problematic

quantification of maleic and fumaric acid, even though these acids could be detected. The other diacids of the realistic scenario could be readily quantified.

With the separation of the higher concentrations obtained by Ho *et al.* (2006) (Appendix C, Chromatograms C.5 and C.6) both the ideal and realistic scenarios' quantification and detection of the diacids were quite good. The only incident worth mentioning was of fumaric acid eluting as the smallest peak in the realistic scenario, but this was to be expected since it is the least abundant diacid out of the specified 7 diacids. Also, maleic acid overlapped marginally with nitrate.

In summary, separation of the dicarboxylic acid concentrations specified by Virtual Column was the best out of the three concentration scenarios. But even if the concentrations of the ambient aerosol filters should prove to be comparable with those of the literature low, and high values, detection and quantification would still be possible.

4.2.5. Conclusion

The optimum column, temperature and eluent program which was now established will be applied next. The ICS-3000 RFIC with column AS18 (2x250mm), set at a temperature of 30°C and gradient elution program used in chromatogram B.8 Appendix B, will be applied to:

1. The 7 dicarboxylic acid (C_2, C_3, C_4, C_5, Ph, F and M) and inorganic ion standards (fluoride, chloride, nitrate and sulphate), made up in 2 mg/l concentration solutions firstly as;
   - Individual compounds,
   - Secondly as a solution containing all 7 dicarboxylic acids and lastly;
   - As a solution containing all dicarboxylic acids and inorganic ions.

2. After establishing if the conditions are practically applicable, the IC methodology will be used to analyze the extracted WSOC from the Vaal Triangle ambient aerosol filters.

The concentrations of the filter dicarboxylic acids are expected to be in the range obtained in Ho *et al.'s* 2006 study, which were lower than the designated Virtual Column's values. With this in mind, first a single filter and then combined filter extracts of two and more will be extracted and analyzed, until purposeful dicarboxylic acid detection and separation are achieved.

4.3. FIELD CAMPAIGN RESULTS

4.3.1. Ion chromatography methodology

From the above section (Paragraph 4.2.2.8; 4.2.3.4 and 4.2.4) dicarboxylic acid and inorganic ion separation conditions were simulated with the software, Virtual Column. It was concluded that the ICS-3000 RFIC with IonPac column AS18 (2x250mm), set at a column temperature of 30°C, utilizing gradient elution (starting eluent concentration value of 10 mM and gradient slope 0.300 mM/min) and 2 mg/l dicarboxylic acid and inorganic ion solutions were to be used.

4.3.1.1. Individual dicarboxylic acid analysis

The first step was to analyze test samples of the 7 dicarboxylic acids (C_2-C_5, Ph, M and F) individually (Appendix D, Chromatograms D.1-D.7) according to the new methodology. This was done in order to obtain the retention times at which each diacid would elute (Table 4.17). These retention values were initially compared with the retention times found with the Virtual Column simulation separator (Appendix B, chromatogram B.8). However, the 7 dicarboxylic acids were simulated as a mixture with the inorganic ions and thus the retention times of the simulation could differ from those obtained for the test samples by ICS-3000 RFIC.

Table 4.17: Retention times of the ICS-3000 RFIC individually separated dicarboxylic acids and Virtual Column's simulated dicarboxylic acid and inorganic ion mixture.

Dicarboxylic acid		Virtual Column Dicarboxylic and inorganic mixture (minutes)	ICS-3000 RFIC (minutes)
Oxalic	C_2	28.20	19.97
Malonic	C_3	23.76	15.77
Succinic	C_4	22.08	16.68
Glutaric	C_5	22.95	16.46
Maleate	**M**	19.15	17.53
Fumaric	**F**	35.25	25.49
Phthalic	**Ph**	51.16	37.16

As can be seen from Table 4.17, the retention times of the simulation and experimental separations with the ICS-3000 RFIC did differ. The diacids eluted sooner than the values predicted by Virtual Column. Also, the order of elution obtained from the simulation were: M, C_4, C_5, C_3, C_2, F and Ph whereas ICS-3000 RFIC eluted the diacids as: C_3, C_5, C_4, M, C_2, F and Ph.

In the next step the 7 dicarboxylic acids were separated as a solution. The order of separation could possibly change to represent that of Virtual Column, depending on the influence the diacids have on each other when being separated as a solution.

4.3.1.2. Dicarboxylic acid mixture analysis

Next, a test solution containing all seven dicarboxylic acids were separated (Table 4.18). The chromatogram can be seen in Appendix D, D.8.

Table 4.18: ICS-3000 RFIC retention values of the dicarboxylic acid mixture solution.

Dicarboxylic acid		Virtual Column Dicarboxylic and inorganic mixture	ICS-3000 RFIC Individual	ICS-3000 RFIC Mixture
		minutes		
Oxalic	C_2	28.20	19.97	20.46
Malonic	C_3	23.76	15.77	16.69
Succinic	C_4	22.08	16.68	16.69
Glutaric	C_5	22.95	16.46	16.69
Maleate	**M**	19.15	17.53	18.32
Fumaric	**F**	35.25	25.49	25.64
Phthalic	**Ph**	51.16	37.16	37.27

From Table 4.18 and chromatogram D.8 it is immediately apparent that there were 5 and not seven peaks, as was expected. Also, the retention times of the mixture differed from the mixture simulated by Virtual Column, but closely resembled the values of the individual compounds.

The first eluted peak (16.69 min; marked in green) was rather broad and most probably contained compounds C_3, C_4 and C_5. This however could have been expected when looking at the individual retention times (C_3: 15.77, C_5: 16.46 and C_4: 16.68 min). Even with Virtual Column, although the retention values of C_3, C_4 and C_5 were spaced approximately one minute apart, chromatogram B.8 showed a simulated chromatogram with compounds C_3, C_4 and C_5 barely separated. The rest of the compounds (M, C_2, F and Ph) eluted as sharp peaks with only M potentially being problematic, eluting close to the peak containing C_3, C_4 and C_5.

The final step was to combine the 4 inorganic ions simulated by Virtual Column with the 7 dicarboxylic acids in a solution. Although up to this point the experimental and simulated results differed in separation order and retention values, the inorganic ions could possibly change the separation results further.

4.3.1.3. Individual inorganic ion and mixture analysis

The four commonly found ambient inorganic ions, fluoride, chloride, nitrate and sulphate were analyzed individually (Table 4.19) to obtain retention times and predict if a possible overlap with the dicarboxylic acids would occur. Chromatograms can be seen in Appendix D, D.9-D.12. Then, a solution containing the dicarboxylic acids as well as the inorganic ions (Appendix D, Chromatogram D.13) was analyzed and compared with the simulated Virtual Column separation (Appendix B, Chromatogram B.8). This can also be seen in Table 4.19.

Table 4.19: ICS-3000 RFIC inorganic ion and dicarboxylic acid mixture analysis.

Compounds		Virtual Column	ICS-3000 Individual	ICS-3000 Organic mixture	ICS-3000 Organic & inorganic mixture
		minutes	minutes	minutes	minutes
Fluoride		4.78	4.55	-	4.55
Chloride		8.18	6.72	-	6.69
Nitrate		18.69	12.71	-	12.68
Sulfate		23.88	17.16	-	17.01
Oxalic	C_2	28.20	19.97	20.46	20.56
Malonic	C_3	23.76	15.77	16.69	17.01
Succinic	C_4	22.08	16.68	16.69	17.01
Glutaric	C_5	22.95	16.46	16.69	17.01
Maleate	M	19.15	17.53	18.32	18.42
Fumaric	F	35.25	25.49	25.64	25.77
Phthalic	Ph	51.16	37.16	37.27	37.41

It was now clear that the real separation differed somewhat from the simulation with compounds eluting prior to the values predicted by Virtual Column. A problematic result was the single peak elution of possibly C_3 C_4, C_5 and sulphate as indicated in green in Table 4.19. Also, compounds M, C_2, F and Ph eluted as broad peaks and not the well defined peaks usually obtained by gradient elution and simulated by Virtual Column. However, the simulation and the ICS-3000 RFIC separation did correlate on the order and retention times of inorganic ions fluoride, chloride and nitrate. These three inorganic ions eluted first and would not interfere with the

dicarboxylic acid separation. The values obtained from the single analysis of the organic acids and inorganic ions also closely resembled the values from the mixture analysis, making it probable that the peak which eluted at 17.01 minutes could contain C_3, C_4, C_5 and sulphate.

In conclusion, the differences in the simulated and experimental separations could possibly have been attributed to several factors. Indeterminate errors (accidental or random errors) which represent the experimental uncertainty that occurs in any measurement as well as a possible determinate error. This is a possible explanation since the separation of aerosol dicarboxylic acids was a newly developed method. With possible further studies and method optimization the error could be detected and corrected to result in a separation chromatogram where the simulation and the experimetnal results could be comparable.

However, for this study the next step was to vary the gradient program obtained in the above sectio in order to achieve better separation. This especially meant possibly obtaining the 3 peaks predicted by Virtual Column (C_3 and sulphate, C_5 and C_4) as well as sharp peaks for M, C_2, F and Ph.

4.3.2. Gradient elution

A change in the eluent concentration during an analysis is referred to as a gradient (Reagent-free™ controller operator's manual 2004). Usually the eluting power of the solvent is increased to accelerate the elution of the later eluting substances (Tutorial and User manual Chromeleon 2004).

To set up a gradient, the starting concentration, gradient time and final concentration needs to be specified. The gradient time refers to the number of minutes needed to reach the final concentration, which can be either higher or lower than the starting concentration. The most common gradient (linear gradient), is when a uniform change in the eluent concentration over a specified time is achieved (Reagent-free™ controller operator's manual 2004). An example of a linear ramp gradient with a starting concentration of 30 mM, gradient time of 10 minutes and final concentration

of 60 mM can be seen in Figure 4.6 (Reagent-free^{TM} controller operator's manual 2004).

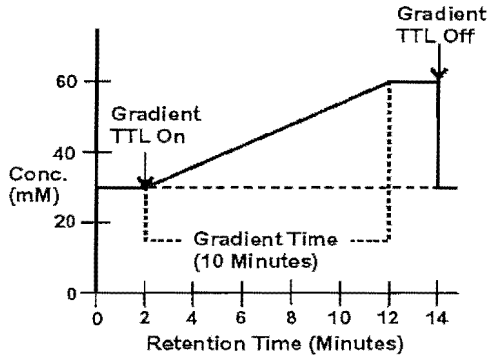


Figure 4.6: *Gradient example (Reagent-free^{TM} controller operator's manual 2004).*

To generate a gradient the solvent value determined for the time is continually adjusted to the solvent command. If the two values coincide, the solvent value is kept at a specific level (Figure 4.7 (a) ramp profile $t_{(0)}$ - $t_{(1)}$). If they differ from each other, the value is modified. The difference between the two time values corresponds to the length of the ramp (Figure 4.7 (a) ramp profile $t_{(1)}$ - $t_{(2)}$) (Tutorial and user manual Chromeleon 2004).

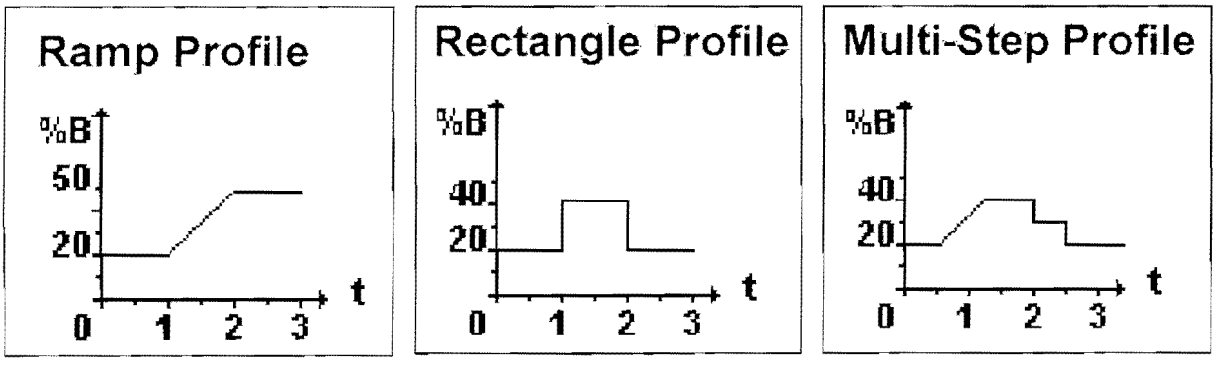


Figure 4.7: *Ramp (a), rectangle (b) and multi-step (c) gradient profile (Tutorial and user manual Chromeleon 2004).*

Gradual (a), immediate (b) or multi-step (c) changes in the eluent concentration can be achieved (Figure 4.7). A multi-step gradient profile is when the ramp and rectangle profile are combined. Continually changing the composition of the delivered solvent mixture over the desired time is referred to as a ramp (or more precisely as a ramp gradient). Contrary to this, immediate changes of the solvent composition are referred to as step gradient. In the case of step gradients, the elution conditions change rapidly (Tutorial and user manual Chromeleon 2004).

In the following section, the gradient elution program simulated by Virtual Column ($t_{(0)}$ = 10 mM, gradient slope = 0.300 mM/min) will be changed to determine which conditions will result in the overlapped peak being separated and the compounds to elute as sharper peaks than was the case with chromatogram D.13 (Paragraph 4.3.1.3).

4.3.3. Varying gradient elution

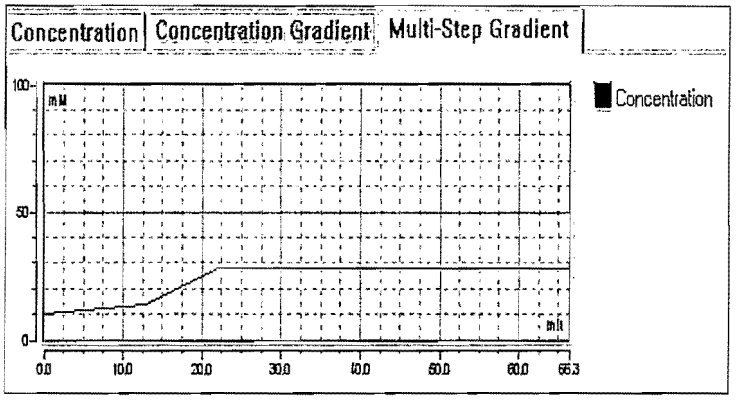
In order to improve the separation of the inorganic ion and dicarboxylic acid mixture (Paragraph 4.3.1.3), a number of gradient programs were tested. There were seven chromatograms (Appendix D, Chromatograms D.14-D.20) which gradient programs produced separations which were significant either as an improvement or deterioration. The gradient programs were: gradient numbers 2, 4, 5, 14, 15, 17 and 21.

Figure 4.8 shows the superimposed resulting chromatograms with the broad overlapped peak (containing possibly sulphate, C_3, C_4 and C_5) marked in green. Progress or deterioration in the separation of the green encircled peak can be seen as the gradient programs from number 2 to 21 are illustrated. The gradient programs as well as the eluent profiles of the seven chromatograms are shown in Table 4.20.

Table 4.20: Gradient programs and eluent profiles of the varying eluent separations.

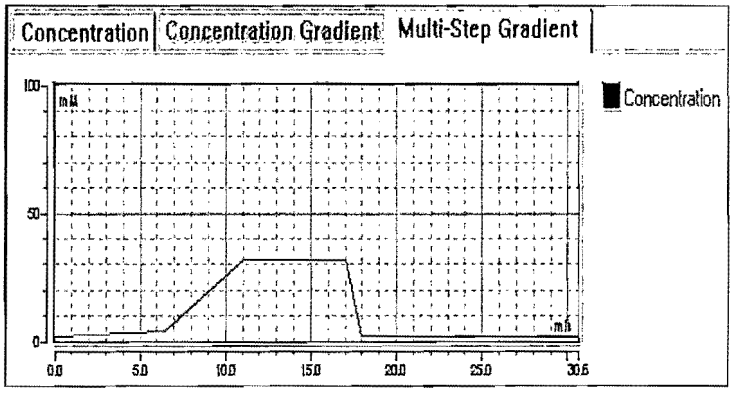
Gradient program nr 2	
Time (min)	**Eluent (mM)**
0	10.00
13	14.00
22	28.00
65	28.00

ICS-3000 RFIC Gradient profile



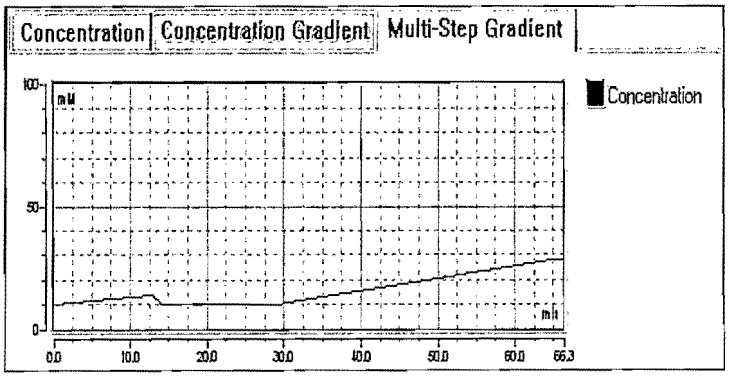
Gradient program 4	
Time (min)	**Eluent (mM)**
0	1.50
6.5	4.00
11	32.00
17	32.00
18	1.50
30	1.50

ICS-3000 RFIC Gradient profile



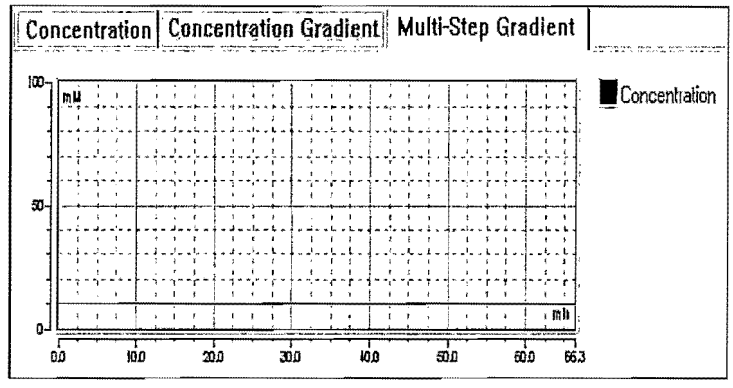
Gradient program 5	
Time (min)	**Eluent (mM)**
0	10.00
13	14.00
14	10.00
29	10.00
65	28.00

ICS-3000 RFIC Gradient profile



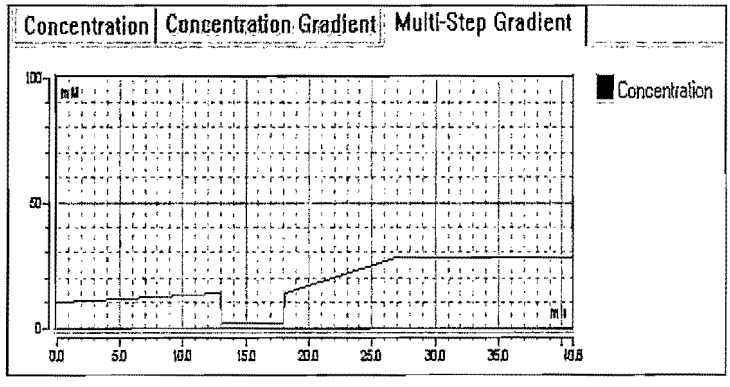
Gradient program 14	
Time (min)	Eluent (mM)
0	10
65	10

ICS-3000 RFIC Gradient profile



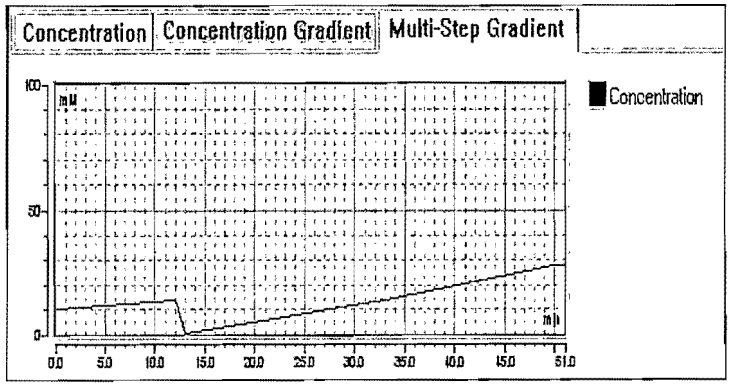
Gradient program 15	
Time (min)	Eluent (mM)
0.000	10
13.000	14
13.100	2
18.000	2
18.100	14
27.000	28
40.000	28

ICS-3000 RFIC Gradient profile

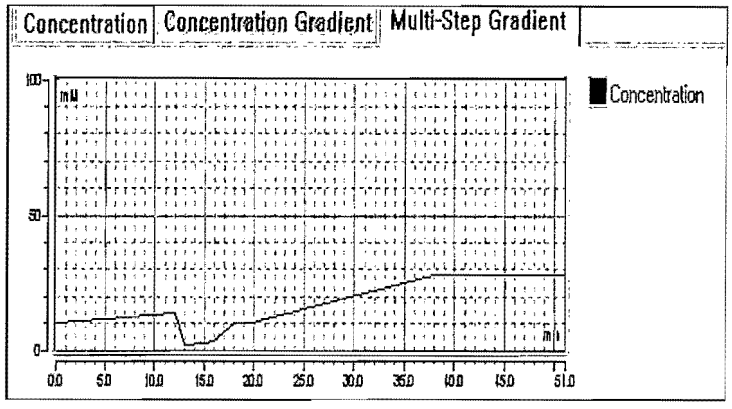


Gradient program 17	
Time (min)	Eluent (mM)
0	10.00
12	14.00
13	0.50
33	14.00
50	28.00

ICS-3000 RFIC Gradient profile



Gradient program 21		ICS-3000 RFIC Gradient profile
Time (min)	Eluent (mM)	
0	10.00	
12	14.00	
13	1.50	
15	2.50	
16	3.50	
18	10.00	
20	10.00	
21	11.50	
38	28.00	
50	28.00	



4.3.3.1. Gradient program number 2

The gradient program was a ramp gradient and showed an improved separation compared to the separation of the Virtual Column spesified program (Table 4.20.; Appendix D, Chromatogram D.14). The last four peaks: maleate (18.47 minutes), oxalate (20.04 minutes), fumarate (23.03 minutes) and phthalate (28.21 minutes) were sharper and better defined as well as Ph and F eluting closer together. Also, M, C_2, F and Ph eluted earlier than was the case with the separation of chromatogram D.13 (M: 18.42, C_2: 20.56, F: 25.77 and Ph: 37.41 minutes). Gradient program 2 had a shorter run time, lasting approximately 30 minutes whereas chromatogram D.13 had a run time of 40 minutes. The broad overlapping peak at 17.19 minutes was still unchanged except for being marginally sharper and closer spaced.

From this program it could be seen that to increase the eluent concentration for the first 13 minutes from the starting value of 10 to 14 mM, the perfect separation of fluoride, chloride and nitrate would be obtained. The three compounds eluted as sharp and well defined peaks. The next step was then to change the gradient program to elute the remaining compounds further apart with no overlap.

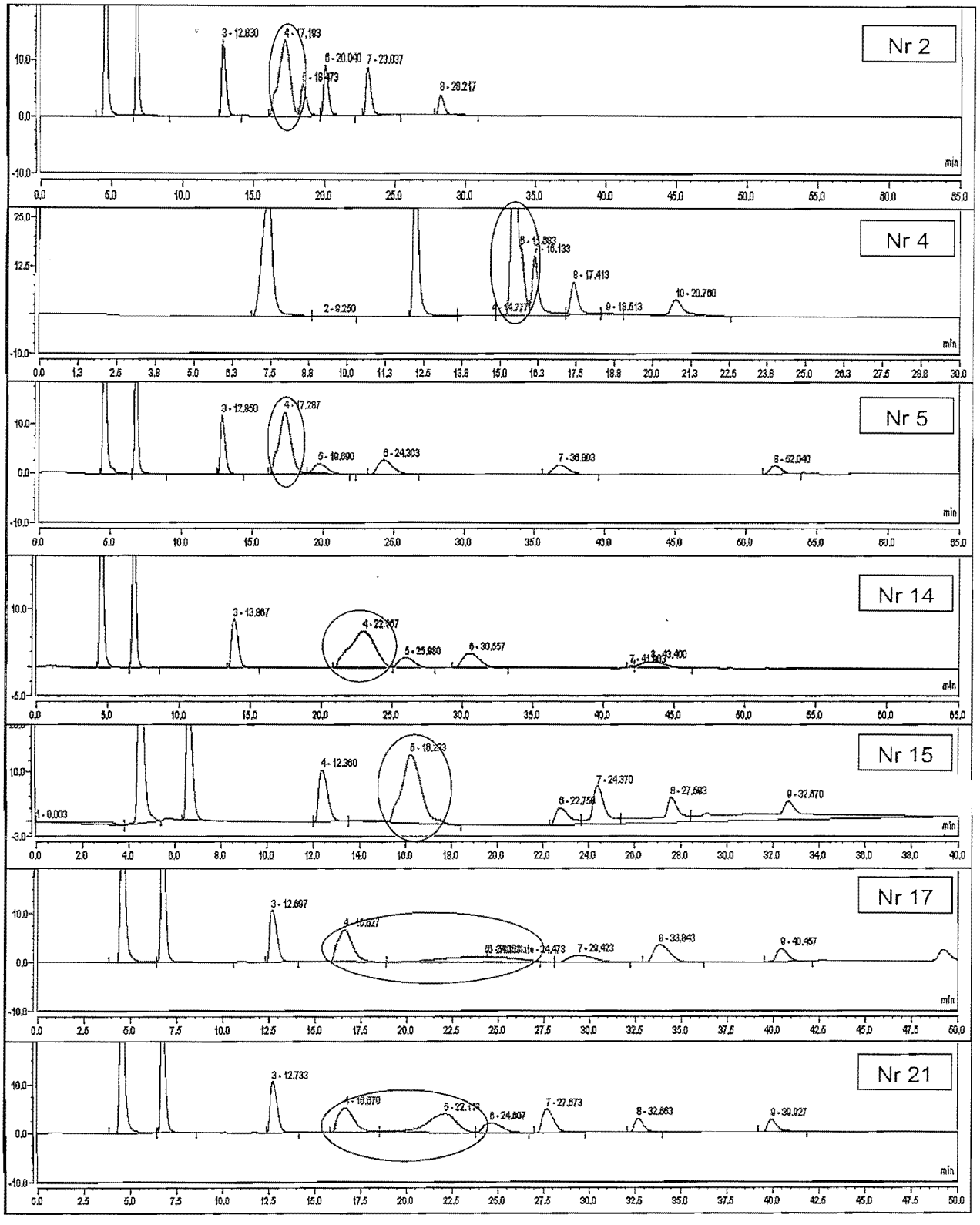


Figure 4.8: *Superimposed chromatograms of the continual improved gradient programs.*

4.3.3.2. Gradient program number 4

This gradient program was a multi-step gradient (Figure 4.8, Table 4.20) and in this case produced a worse chromatogram. The first two inorganic ions, fluoride and chloride, seemed to have eluted as one peak (7.41 minutes) and sulphate, C_3, C_4 and C_5 as a sharp and closely spaced peak (15.45 minutes). Furthermore, only three, and not four peaks eluted after the overlapped peak of sulphate, C_3, C_4 and C_5. This probably meant that either maleate also overlapped with the peak marked in green or that phthalate, or possibly fumarate, did not elute. This could have been the case due to the separation time being only 30 minutes. Also, the eluent concentration was rapidly decreased from $t_{(17)}$ = 32 mM to $t_{(18)}$ = 1.50 mM, possibly retaining F or Ph on the column.

The eluent concentration also reached a higher concentration earlier in the gradient program ($t_{(11)}$ = 32 mM) than Virtual Column simulated ($t_{(60)}$ = 28 mM). This confirmed that the eluent concentration should not exceed the maximum value assigned by Virtual Column.

From this program it was discovered that shortening the run time, quickly increasing the eluent concentration and then drastically lowering the concentration, was not to be recommended. Increasing the eluent concentration quickly to such a high level made the compounds elute closer together, causing overlap and a bad separation. Thus, gradient program number 2 proved the better separation thus far and was the program to improve upon.

4.3.3.3. Gradient program number 5

This program was mostly a ramp gradient (Table 4.20) and resulted in a worse separation than obtained with gradient program number 2. The overlapped peak (marked in green in Figure 4.8) was unchanged whereas the four last eluting peaks; M, C_2, F and Ph were now broad and further spaced from each other. Lowering the eluent concentration from $t_{(13)}$ = 14 mM to the starting value of 10 mM at $t_{(14)}$, and then keeping the concentration constant for 15 minutes, only broadened the peaks and made the compounds elute further apart.

Thus, the eluent concentration should be lowered after 13 minutes to pull apart the green overlapped peak but should not be kept constant (isocratic) at 10 mM. Also, to obtain sharp and well defined M, C_2, F and Ph peaks, a higher eluent concentration than 10 mM should be reached earlier in the separation than 29 minutes, as was the case in this study.

4.3.3.4. Gradient program number 14

This gradient program was an isocratic separation of 10 mM (Table 4.20) and supported the Virtual Column simulation that the inorganic ion and dicarboxylic acid mixture could only be separated effectively with gradient elution. Three compounds, instead of the expected four, seemed to have eluted after the overlapped peak of 22.96 minutes (Figure 4.8). These compounds also eluted as broad and badly defined peaks. The fact that there appeared to have been only three peaks could be that two compounds had eluted as one peak (F and Ph) or that a peak had not eluted at all (Ph). The former seemed likely because the RFIC software, Chromeleon, registered 4 peaks with retention times (25.98, 30.55, 41.90 and 43.40 minutes). The last two compounds probably eluted as very broad peaks and possibly overlapped, appearing as one peak.

However the isocratic separation did prove useful; it managed to spread out the overlapped peak of 22.96 minutes. This meant that by starting at a lower concentration after the first three inorganic ions were separated at $t_{(13)}$ = 14 mM (as in gradient program number 2) continuing with a ramp gradient could possibly pull the overlapped compounds further apart.

4.3.3.5. Gradient program number 15

This gradient program was a multi-step program and was the first program to improve on the separation of gradient program number 2. The last four peaks (M: 22.75, C_2: 24.37, F: 27.59 and Ph: 32.67 minutes) eluted well spaced from each other as well as separately from the overlapped peak (16.23 minutes). This showed promise, indicating that the overlapped peak's compounds eluted at a lower eluent

concentration (2 mM) than did M, C_2, F and Ph (approximately 20 mM and higher). Also the overlapped peak seemed broader, indicating that the compounds were probably starting to elute separately.

Interesting to note, the shorter separation time (40 minutes) did not affect the separation negatively. That was because after lowering the eluent concentration to 2 mM and keeping it constant for 4.9 minutes, the concentration was increased (1.57 mM/min) according to the specifications of gradient program number 2 (1.55 mM/min)

4.3.3.6. Gradient program number 17

This ramp gradient (Table 4.20) was the first gradient program to elute the overlapped peak into two definable peaks, with Chromeleon registering three peaks. The peaks eluted at 16.62, 24.32 and 24.47 minutes, with the last two appearing as one peak. Unfortunately the run time (50 minutes) was too short and Ph did not elute properly. Also, M (29.42 minutes) eluted as a broad peak close to the overlapped peaks of 24 minutes.

What was important from this gradient program was the separation of sulphate, C_3, C_4 and C_5 into two peaks. This was done by lowering the eluent concentration from $t_{(12)}$ = 14 mM to $t_{(13)}$ = 0.50 mM and raising it again to reach 14 mM by 33 minutes at 0.675 mM/min. With the next gradient program the eluent concentration was raised to bring the compounds from the second overlapped peak closer together. This was to determine the starting and end retention times of the two overlapped peaks. Also, raising the eluent concentration would elute M, C_2, F and Ph as sharp peaks.

4.3.3.7. Gradient program number 21

Thus from the previous gradient programs it was determined that for the inorganic ions eluting at the beginning of the separation, the eluent concentration should be 14 mM. After that, in order to separate the overlapped peak possibly containing sulphate, C_3, C_4 and C_5, the concentration should be lowered. Lastly, the eluent

concentration should be raised again to elute M, C_2, F and Ph as sharp and well spaced peaks.

Gradient program number 21 was a multi-step gradient program. From Table 4.20 it can be seen that this was the most elaborate gradient program. Figure 4.8 shows that the overlapped peak was separated into two definable peaks spaced well apart from each other at 16.67 and 22.11 minutes. The first peak was achieved by increasing the eluent concentration from $t_{(16)}$ = 3.50 mM to $t_{(18)}$ = 10 mM by 3.25 mM/min. With the second overlapped peak the eluent concentration was increased from $t_{(21)}$ = 11.50 mM to $t_{(38)}$ = 28 mM by 0.97 mM/min.

Furthermore; C_2 (27.67 minutes), F (32.66 minutes) and Ph (39.92 minutes) did elute as well spaced and sharper peaks. This was because of the increased eluent concentration of 0.97 mM/min between 21 and 38 minutes, as mentioned above, as well as the isocratic eluent concentration of 28 mM after 38 minutes. Unfortunately maleate (24.60 minutes) eluted closely as a broad peak to the overlapped peak of 22.11 minutes.

4.3.3.7.1 Compounds of the overlapped peaks

Throughout the gradient elution of Section 4.3.3, four compounds (sulphate, C_3, C_4 and C_5) were absent each time from the chromatograms. According to Virtual Column's simulation, it was predicted that sulphate (23.88 minutes) and C_3 (23.76 minutes) would elute as one peak and that C_4 (22.08 minutes) and C_5 (22.95 minutes) would elute closely spaced but as separate peaks. The individual analysis however eluted the compounds as: C_3 = 15.77, C_5 = 16.46, C_4 = 16.68 and sulphate = 17.16 minutes. This possibly meant that C_4 and C_5 most likely would elute as one peak with C_3 and sulphate eluting as closely linked peaks prior and subsequently.

The broad peak which eluted with each separation of Section 4.3.3 was assumed to contain the missing 4 compounds. With gradient program number 17 and 21 the peak could finally be separated into two peaks. The four compounds were now individually analyzed (Appendix D, Chromatograms D.21-D.24) according to gradient program number 21 to determine the retention values. Table 4.21 shows these

retention values as well as the values from the inorganic ion and dicarboxylic acid separation first eluted by gradient program number 21 (Appendix D, Chromatogram D.20).

According to the individual analysis of sulphate, C_3, C_4 and C_5 in Table 4.21, the order of elution was sulphate, C_5, C_3 and C_4. The four peaks eluted very close together at around 15 and 16 minutes and could possibly account for the broad peak at 16.67 minutes of the inorganic ion and dicarboxylic acid mixture separation. However, that still left the peak at 22.11 minutes unaccounted for. The only explanation could be that with all seven dicarboxylic acids and four inorganic ions present in a separation, the compounds could influence the elution time of each other and make the compounds elute later. This was seen in a marginal way in Table 4.19, Paragraph 4.3.1.3.

It seems then possible that sulphate and C_5 could elute as one peak and C_3 and C_4 as the other. This coincides with gradient program number 17 where Chromeleon identified 3 peaks at 16.62, 24.32 and 24.47 minutes.

Table 4.21: Sulphate, C_3, C_4 and C_5 retention times in individual and mixture separations.

Compounds		Gradient 21 mixture	Gradient 21 Individual
		minutes	minutes
Fluoride		4.55	
Chloride		6.73	
Nitrate		12.73	
Sulfate		**16.67**	15.71
		22.11	
Oxalic	C_2	27.67	
Malonic	C_3	**16.67**	15.99
		22.11	
Succinic	C_4	**16.67**	16.04
		22.11	
Glutaric	C_5	**16.67**	15.77
		22.11	
Maleate	**M**	24.60	
Fumurate	**F**	32.66	
Phthalate	**Ph**	39.92	

CHAPTER 5
DISCUSSION AND CONCLUSION

In this chapter the results obtained from the Vaal Triangle aerosol filters in Chapter 4 are discussed. The objectives stipulated in Chapter 1 are evaluated and recommendations for further studies are made.

5.1. VAAL TRIANGLE AEROSOL FILTERS

Filters of the winter sampling campaign in July 2006 were analyzed instead of the summer filters of March 2007. This was due to the increased WSOC concentrations in ambient air occurring most probably in the winter, rather than in the summer season. Prominent winter meteorological conditions such as stable layers, reduced wind speed and rainfall typical of the Highveld and in this case, the Vaal Triangle, would contribute to the accumulation of emitted and precursor WSOC's.

Also, in the study by Kleynhans (M.Sc Dissertation 2008) where the spatial and temporal distribution of trace elements in aerosols in the Vaal Triangle were monitored, SEM/EDS results indicated that the carbonaceous particles were the dominant species collected on the TFP filters with the average winter weight percentages of carbon per sample being 52% (range: 24% - 94%) whereas the summer ranged from 7 - 22%. Kleynhans's study was conducted during the same time as this study, at the same locations in July 2006 and March 2007. It could thus be presumed that WSOC and specifically dicarboxylic acids would be more readily found on the winter rather than the summer sampled filters.

Seven filters of the three day winter aerosol sampling campaign, July 2006 were analyzed by the ICS-3000 RFIC according to gradient program number 21 (Paragraph 4.3.3.7.). Theses filters were the filters left over after first performing GC-MS analysis on mostly the PM_{10} winter samples. This was done because the PM_{10} fraction also includes the $PM_{2.5}$ fraction and would have potentially produced higher concentrations of dicarboxylic acids. Thus, when the IC analysis was

performed, mostly $PM_{2.5}$ filter samples remained for the analysis of the Vanderbijlpark, Vereeniging and Sasolburg sampling sites.

Three filters were of Vereeniging ($PM_{2.5}$, Day 2 and 3 and PM_{10}, day 3), three of Sasolburg ($PM_{2.5}$, Day 1 and 2 and PM_{10}, Day 2) and one of Vanderbijlpark ($PM_{2.5}$, Day 2). All the filter samples were prepared for analysis according to the adapted method of Khare *et al.* (1998) (Paragraph 3.5). Each filter was initially wetted with 5 ml Milli-Q water and extracted using ultrasonication for 15 minutes. A further portion of 10 ml Milli-Q water was added and the filter was again sonicated for 15 minutes.

The 3 water extracts of the Vereeniging filter samples were mixed together and analyzed with the ICS-3000 RFIC. This separation would represent Vereeniging. This was also done with the three extracts of Sasolburg while the one extract of Vanderbijlpark was analyzed separately. The 3 filter extracts of individually Vereeniging and Sasolburg were combined because of the small concentrations predicted by literature. It was possible that the concentrations of the dicarboxylic acids from one filter extract would not be high enough for detection with the ICS-3000 RFIC. However, this proved not to be the case as the filter extract of the Vanderbijlpark sample was sufficient to detect the dicarboxylic acids in. Results can be seen in Table 5.1 and the separation chromatograms in Figure 5.1 to Figure 5.3.

Table 5.1: Ambient aerosol filter retention values of the Vaal Triangle monitoring sites.

Filter	Filter information	Peak nr.	Retention time minutes	Possible compound
1	Vanderbijlpark, metalurgical $PM_{2.5}$ (Day 2)	1	5.08	Fluoride
		2	6.56	Chloride
		3	12.17	Nitrate
		4	16.14	Sulfate, C_3, C_4,&C_5
		5	26.57	C_2
		6	37.90	Ph
2	Vereeniging, residential $PM_{2.5}$ (Day 2&3), PM_{10} (Day 3)	1	5.07	Fluoride
		2	6.55	Chloride
		3	12.15	Nitrate
		4	16.04	Sulfate, C_3, C_4,&C_5
		5	26.42	C_2
		6	37.84	Ph
3	Sasolburg, petrochemical PM 2.5 (Day 1&2) PM 10 (Day 2)	1	5.07	Fluoride
		2	6.56	Chloride
		3	12.12	Nitrate
		4	16.04	Sulfate, C_3, C_3,&C_5
		5	26.51	C_2
		6	37.91	Ph

Most of the inorganic ions and dicarboxylic acids were detected in the ambient aerosol samples. Interesting to note was the similar separation pattern obtained with all three monitoring sites, probably indicating the same dicarboxylic acid sources for the metallurgical (Vanderbijlpark), petrochemical (Sasolburg) and residential (Vereeniging) areas. Unfortunately, the separation of possibly sulphate, C_3, C_4 and C_5 was not achieved as the broad peak of all three monitoring sites indicated. Maleate was also not detected and could possibly either have been included in the broad peak, not have eluted at all or it was not present in the air. Fumarate was also not detected and was probably not present in the air. Apart from that, all the peaks except C_2, eluted as sharp peaks of a good separation.

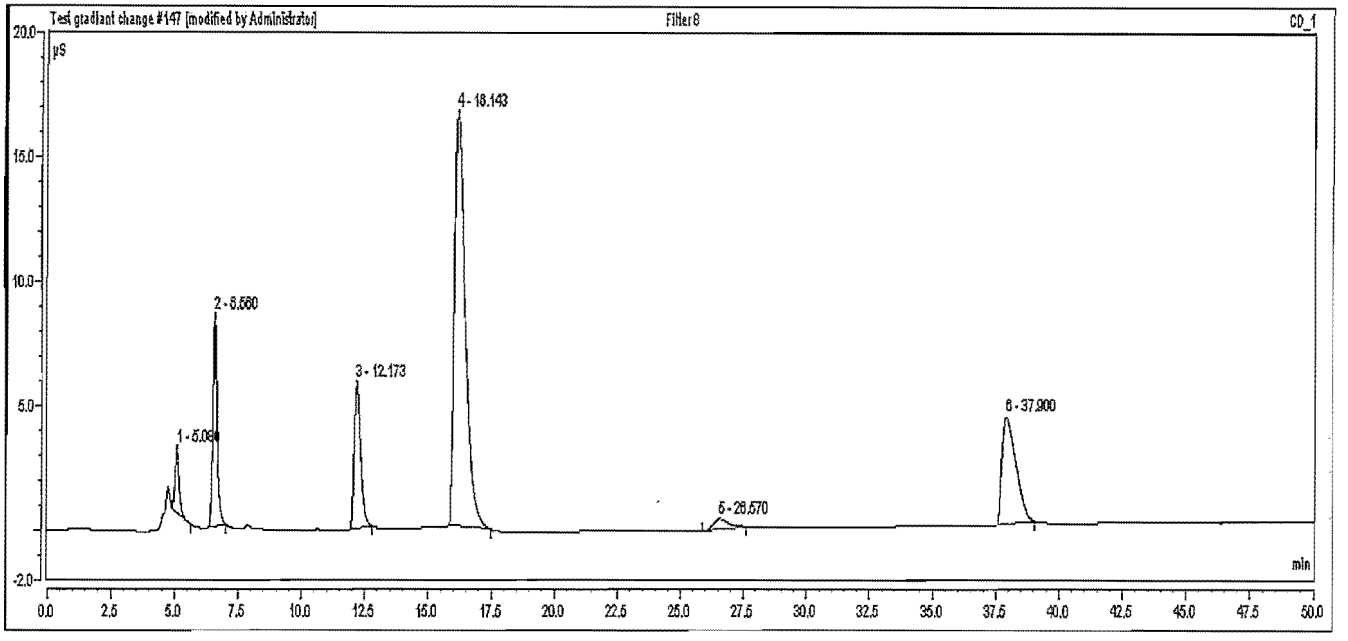


Figure 5.1: *One Vanderbijlpark filter extract eluted with gradient program nr 21.*

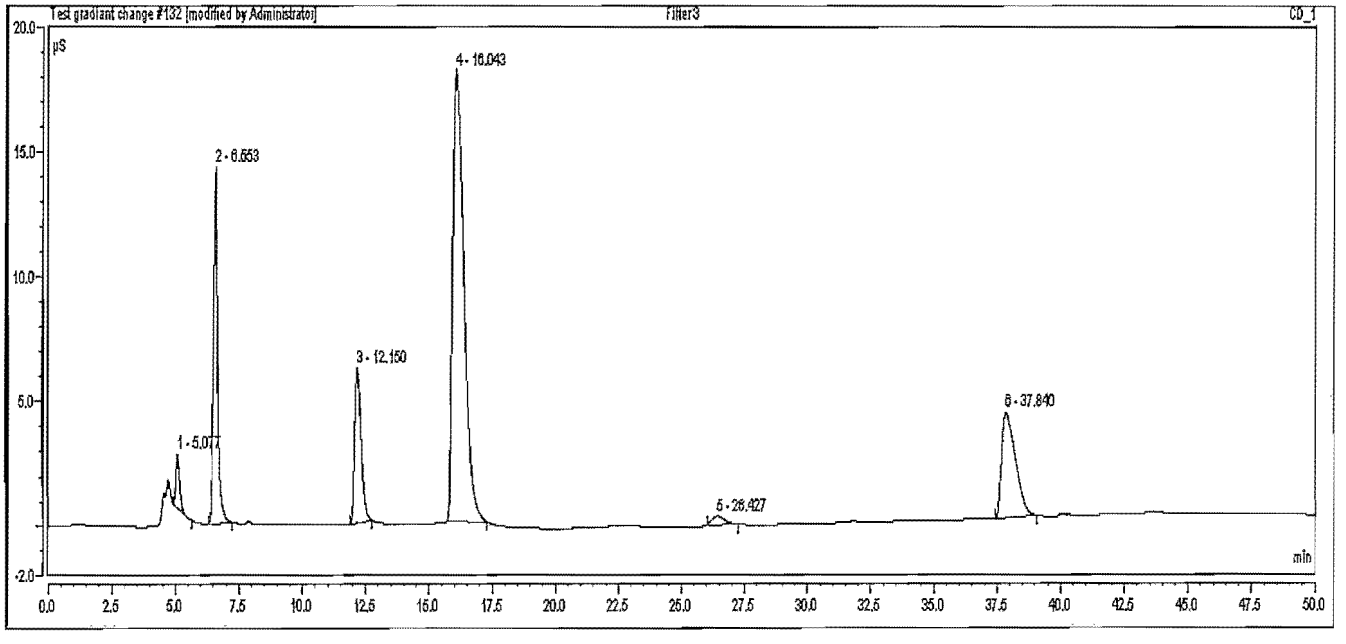


Figure 5.2*: Combined Vereeniging filter extracts eluted with gradient program nr 21.*

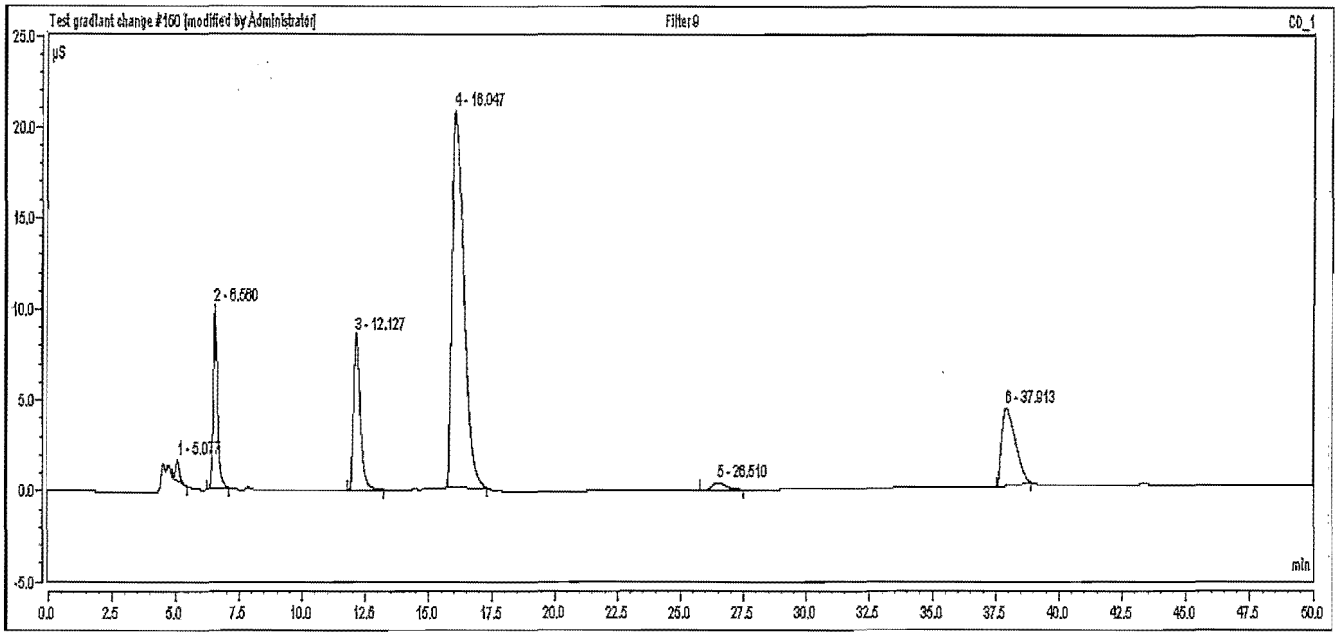


Figure 5.3: *Combined Sasolburg filter extracts eluted with gradient program nr 21.*

Since C_3, C_4, C_5, C_2 and Ph were the possible dicarboxylic acids identified in Chapter 4 with the IC, the sources could be attributed to either primary emitted emissions or secondarily formed by pre-cursor compounds, as mentioned in Chapter 2. According to literature C_3 is formed from the incomplete combustion of fossil fuels and C_2-C_4 dicarboxylic acids produced secondarily from precursors such as unsaturated and saturated hydrocarbons, monocarboxylic acids, aldehydes and keto-acids. Ph has been considered to generate via photochemical oxidation of more specific precursors such as aromatic hydrocarbons and methylcycloalkenes.

Thus, primary dicarboxylic acids and pre-cursor compounds could be from vehicle emissions as well as enhanced biomass burning due to coal combustion in rural areas for warmth and cooking purposes and in industries from combustion purposes. Furthermore, due to the dry season of winter, veldt fires would also be a primary emission source. All of the above also produce pre-cursor compounds for secondary formation of dicarboxylic acids.

5.2. EVALUATION OF THE STUDY OBJECTIVES

The objectives of this study as stated in Chapter 1 could be divided into three sections:

1. To collect PM_{10} and $PM_{2.5}$ fractions at the 3 selected monitoring sites (Vanderbijlpark, Vereeniging and Sasolburg) with MiniVol Portable Air Samplers;
2. To develop a method for qualitative and quantitative analysis of specific dicarboxylic acids applying both GC-MS and IC techniques and
3. To apply the developed method on analyzing the filters sampled in the Vaal Triangle.

The collecting of both winter and summer PM_{10} and $PM_{2.5}$ filter samples was conducted, completing the first objective successfully. However, the methodology development which was the second objective, proved more extensive than was initially thought:

- Possible identification of dicarboxylic acids by GC-MS proved possible but would not be recommended. This technique was able to detect some diacids (C_3, C_4 and C_5) but quantification proved unsuccessful. No dibutylester standards are commercially available which meant that the esters had to be synthesized from dicarboxylic acid standards. This proved ineffective due to the lengthy synthesis pathway and the difficulty of recovering the small concentration.

- Applying IC as a qualitative technique in this study proved to be potentially successful and was the methodology developed as stated in the second objective. The IC method was divided into three sections:

    1. The software Virtual Column was used to create simulations of the compounds to be analyzed, in this case 7 specific dicarboxylic acids. This was done to obtain optimal separation conditions prior to extracting the aerosol filters.

2. The optimized conditions were then further tested and developed by applying the conditions on standard solutions containing both the dicarboxylic acids and 4 inorganic ions.

3. The 7 remaining winter filters, representing all three monitoring sites, were then analyzed according to the methodology developed by the standard solutions. This was the third objective and qualitative data was successfully obtained but unfortunately the method was not further developed to obtain quantitative results.

In conclusion, although no quantitative results could be obtained the study was a success, indicating that dicarboxylic acids are readily present in the ambient air of the Vaal Triangle and that detection and even quantification are possible with an ICS-3000 RFIC.

A concern which arose from the literature study and initial analysis by GC-MS was that, due to the low dicarboxylic acid concentrations (ng/m^3), detection could prove difficult. However this problem was solved with the ICS-3000 RFIC which had no difficulty in detecting the low concentrations.

5.3. RECOMMENDATIONS FOR FUTURE STUDIES

- In future studies it is recommended that the IC methodology be adapted to obtain quantitative as well as qualitative results. For this purpose blank filters should also be analyzed to subtract any possible dicarboxylic acids and inorganic ions present on the filters prior to sampling.

- More frequent, as well as seasonal sampling is recommended. With more samples per season, seasonal trends can be obtained and compared with literature findings.

- Rain samples should be analyzed in conjunction with aerosol samples since the literature indicated that WSOC are more abundant in wet than dry

deposition. This can give an insight on the physicochemical processes or vertical distribution of polar organic compounds in the air column.

- Aerosol samples should be sampled with a high volume sampler as well as a MiniVol in order to see if the results differ significantly, and if more WSOC can be detected.

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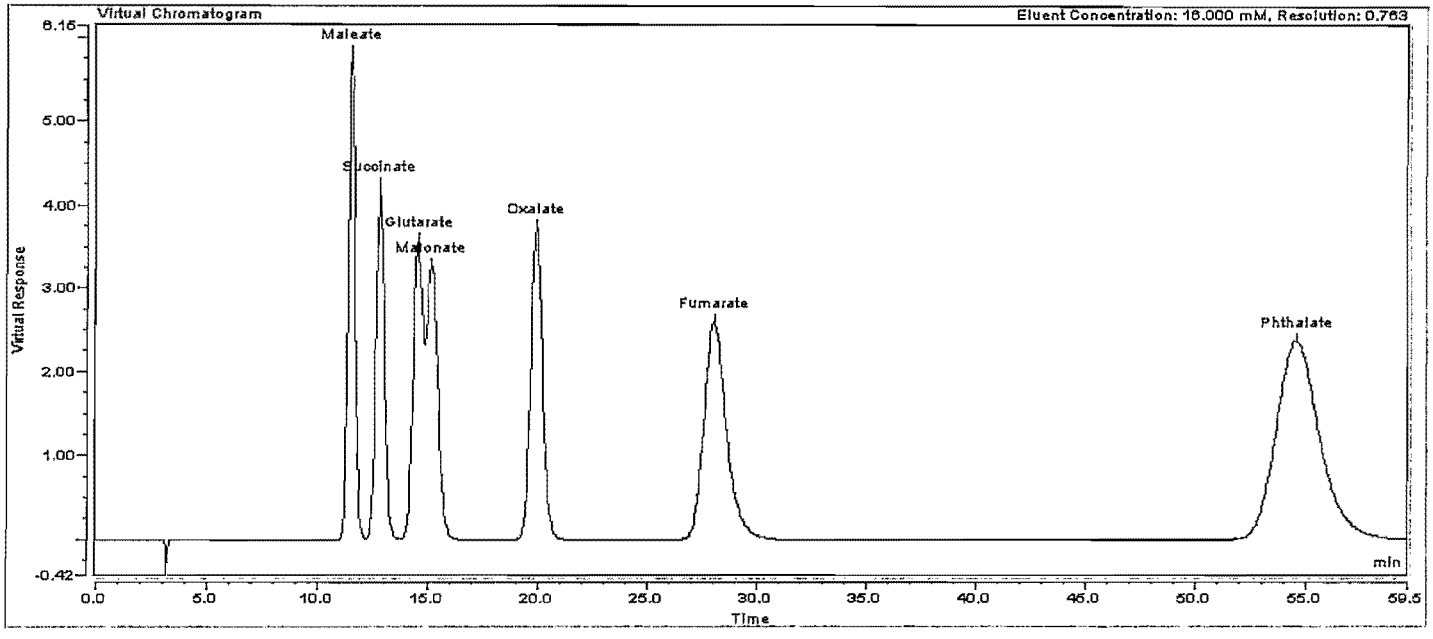
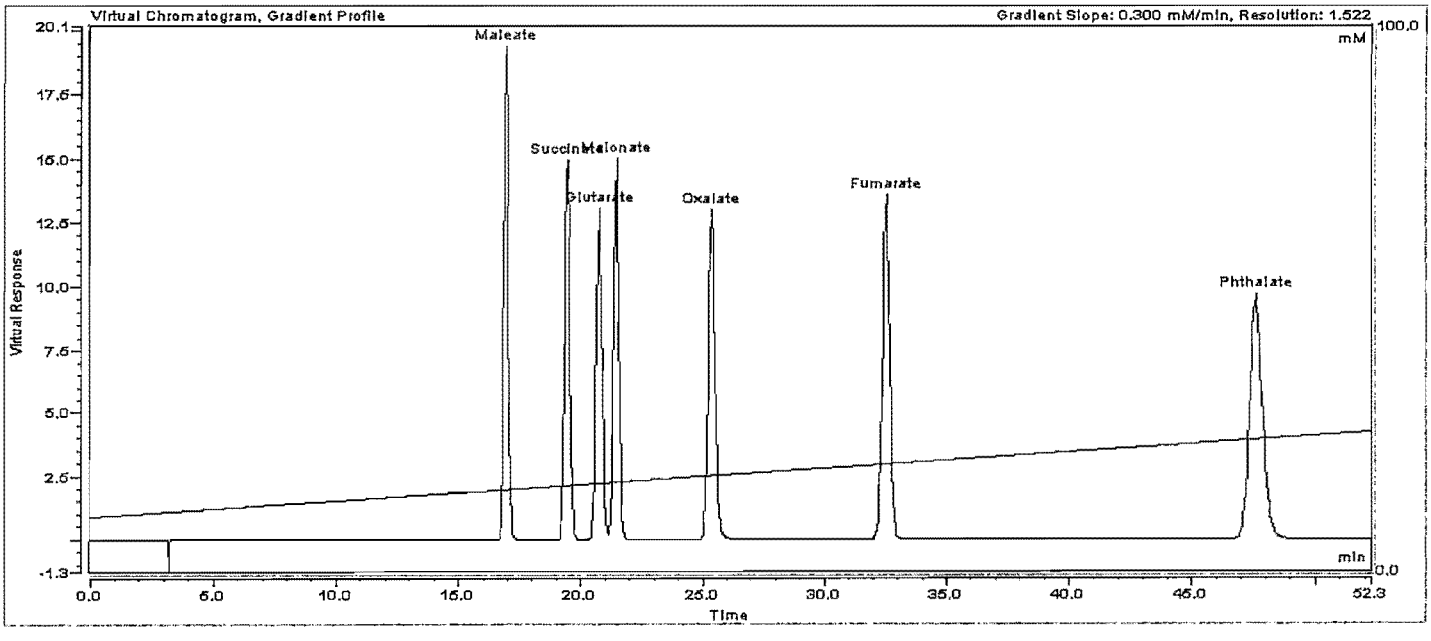
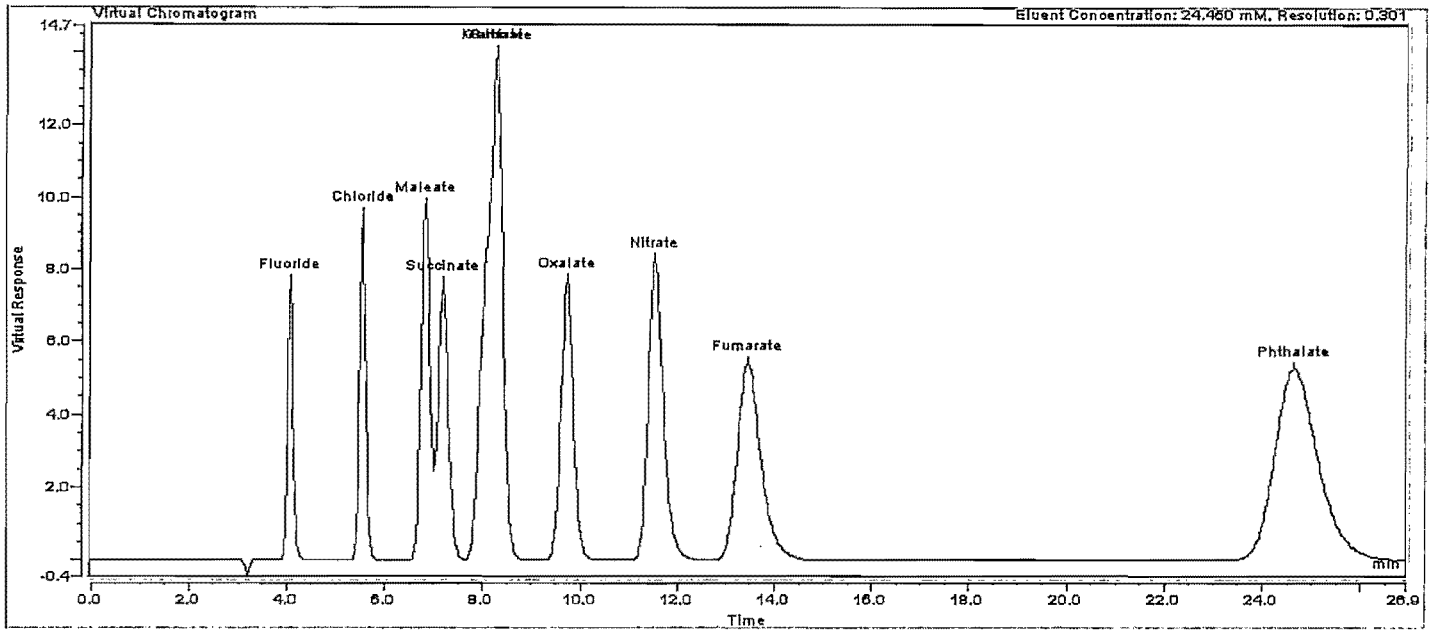
APPENDIX A:
COLUMN SCREENING



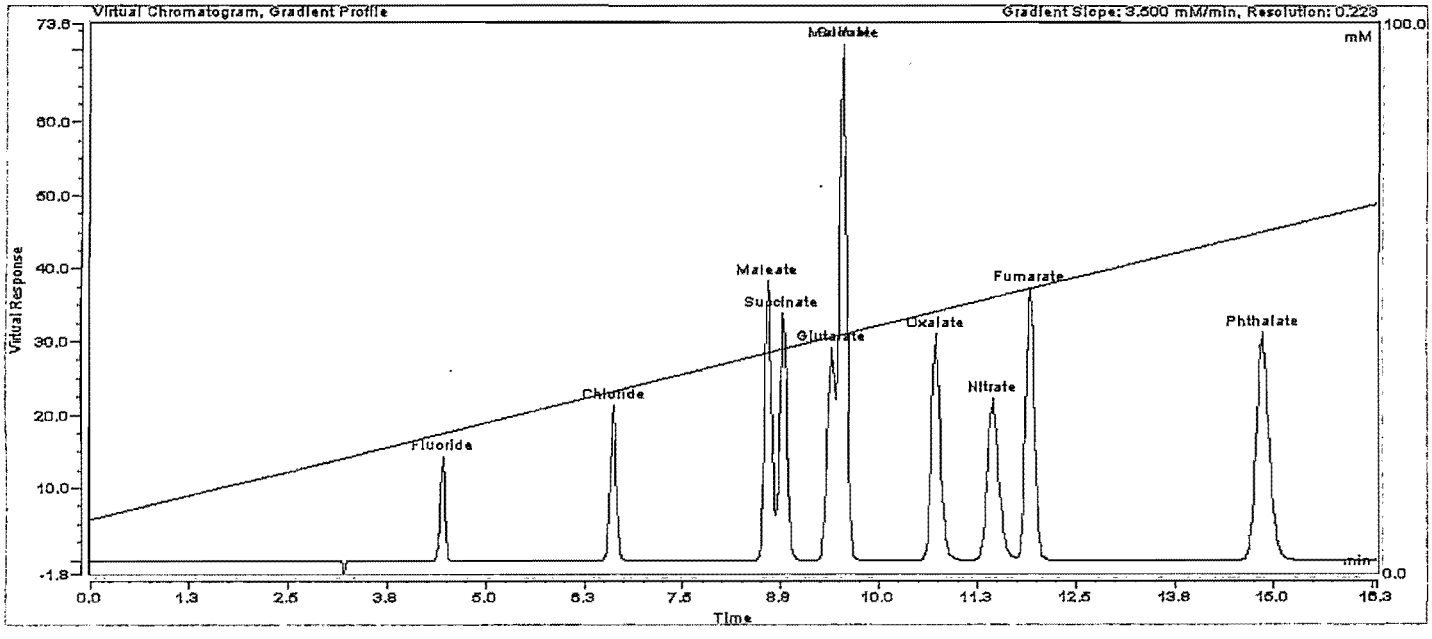
Chromatogram A.1: AS 18 (2x250mm) at 23°C, ideal scenario, isocratic



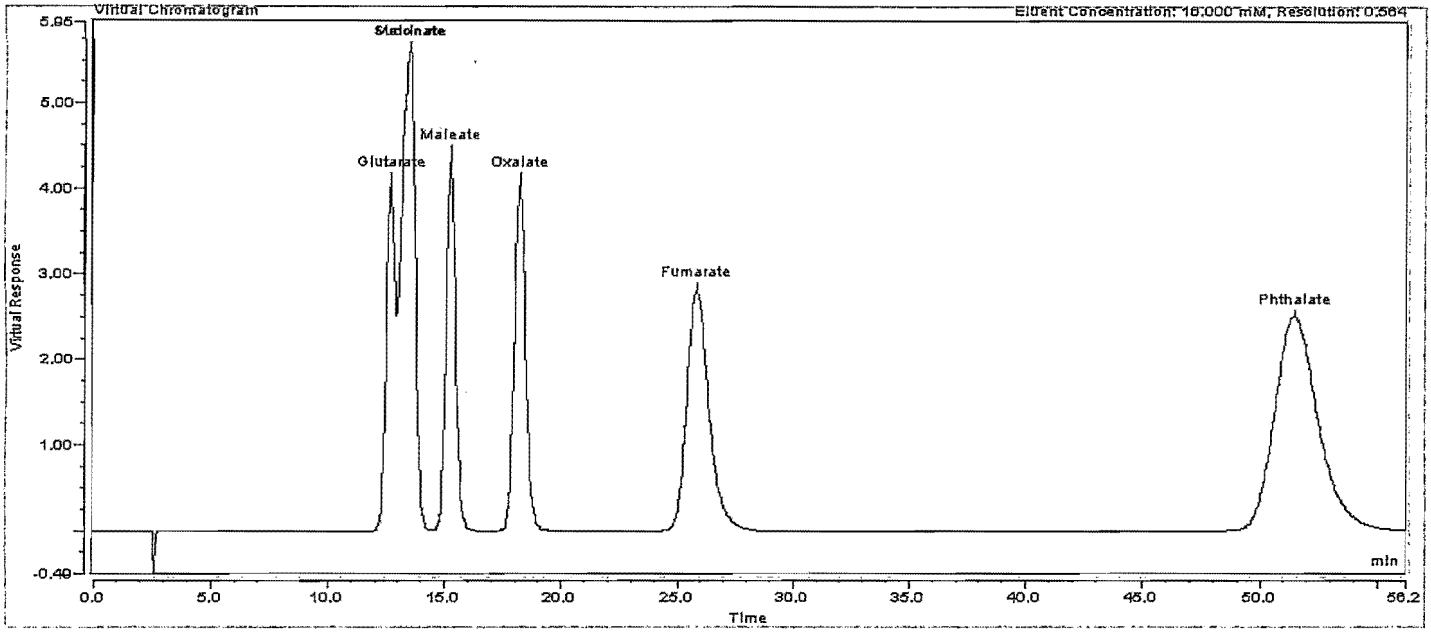
Chromatogram A.2: AS 18 (2x250mm) at 23°C, ideal scenario, gradient



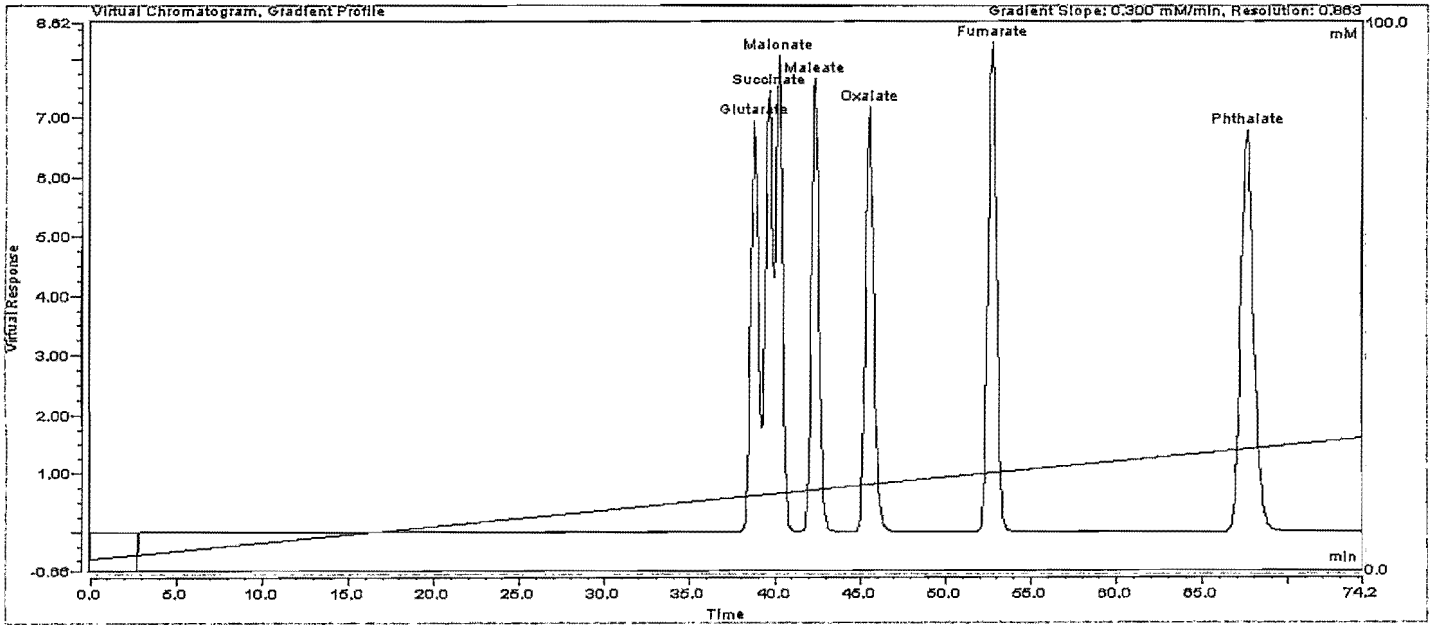
Chromatogram A.3: AS 18 (2x250mm) at 23°C, realistic scenario, isocratic



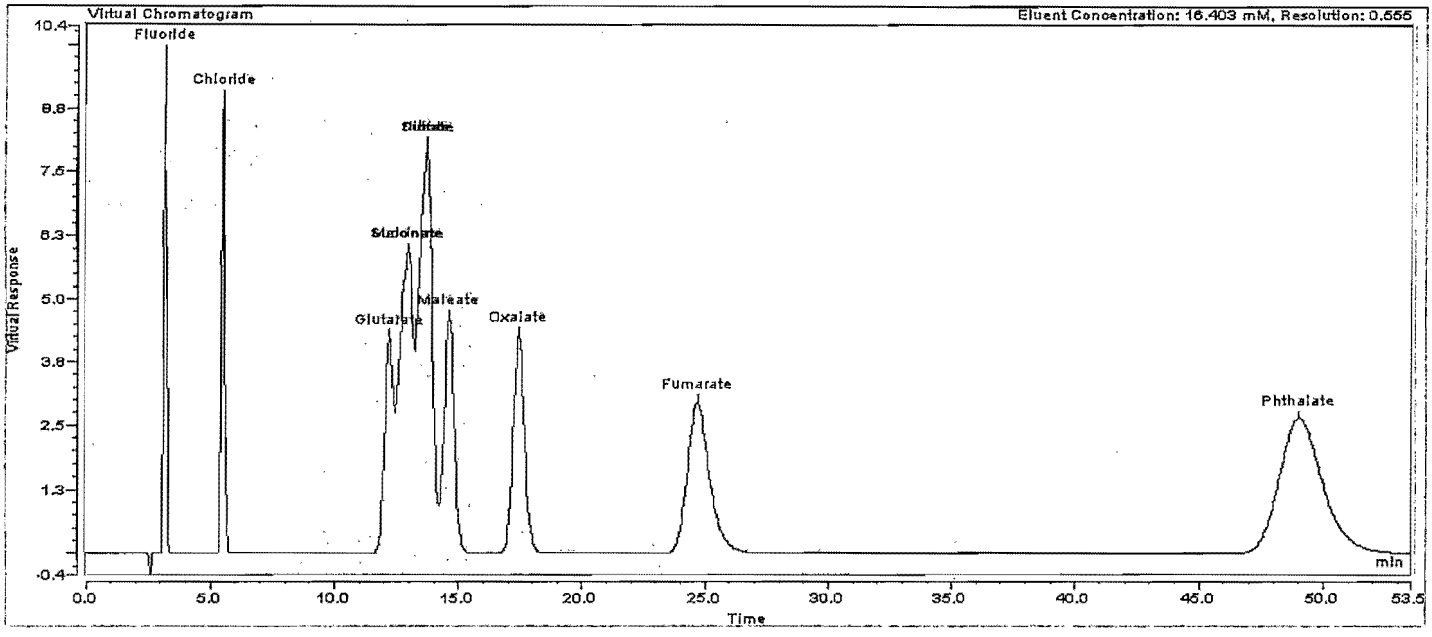
Chromatogram A.4: AS 18 (2x250mm) at 23°C, realistic scenario, gradient



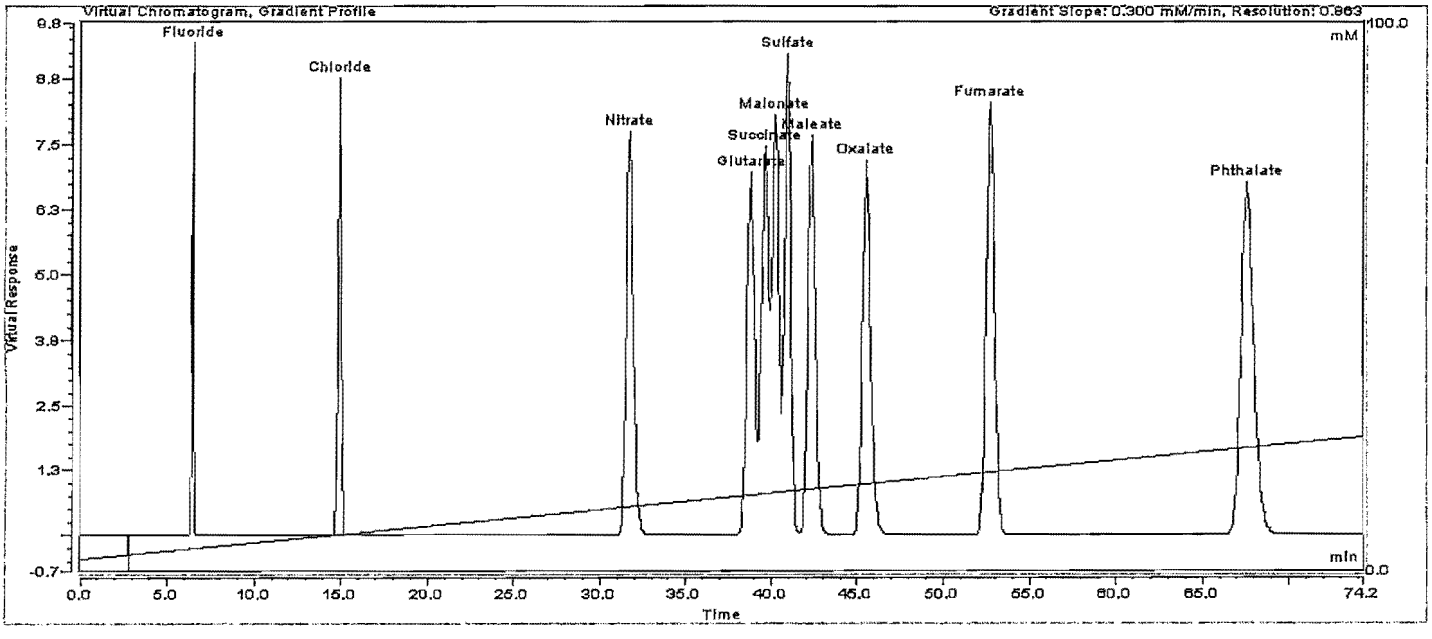
Chromatogram A.5: AS 18 (4x250mm) at 23°C, ideal scenario, isocratic



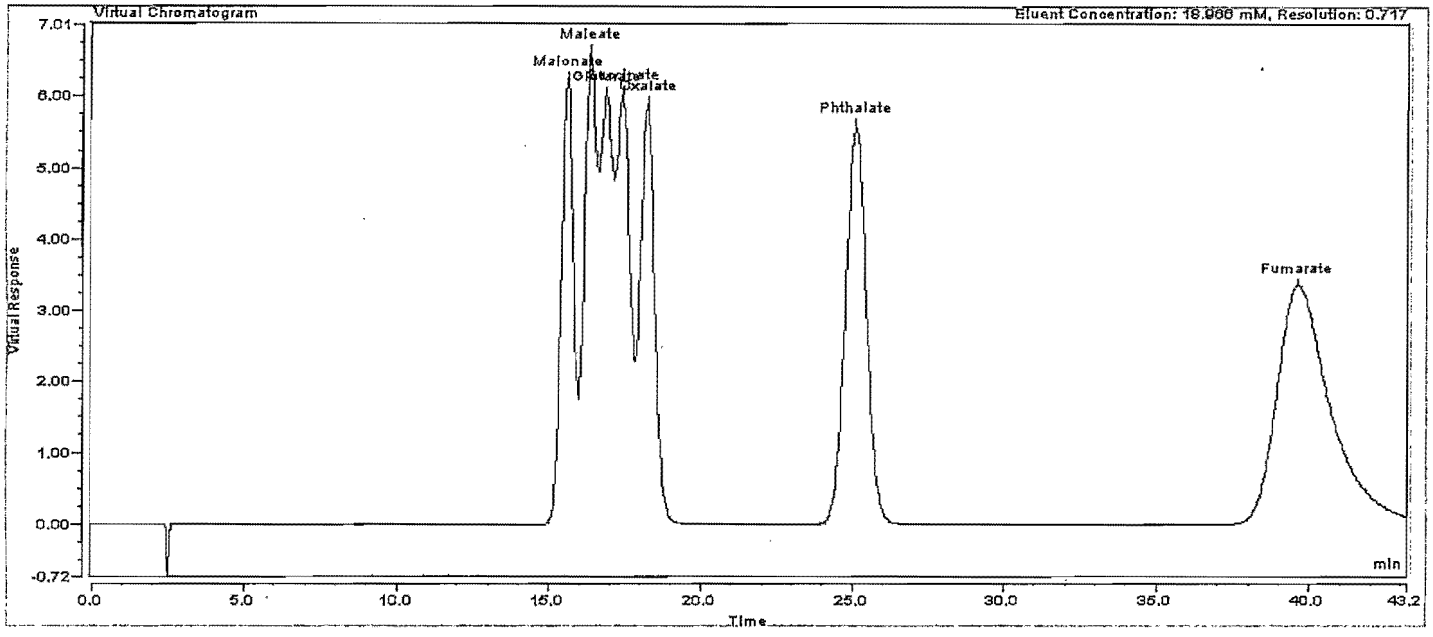
Chromatogram A.6: AS 18 (4x250mm) at 23°C, ideal scenario, gradient



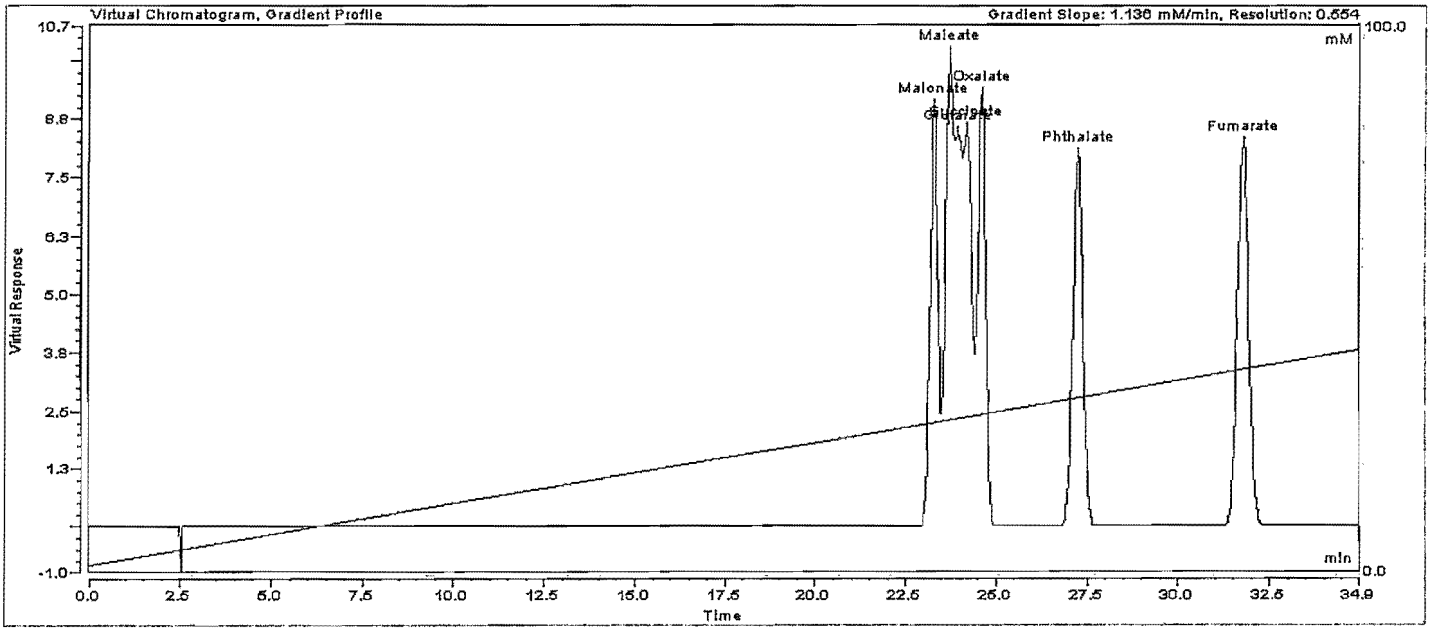
Chromatogram A.7: AS 18 (4x250mm) at 23°C, realistic scenario, isocratic



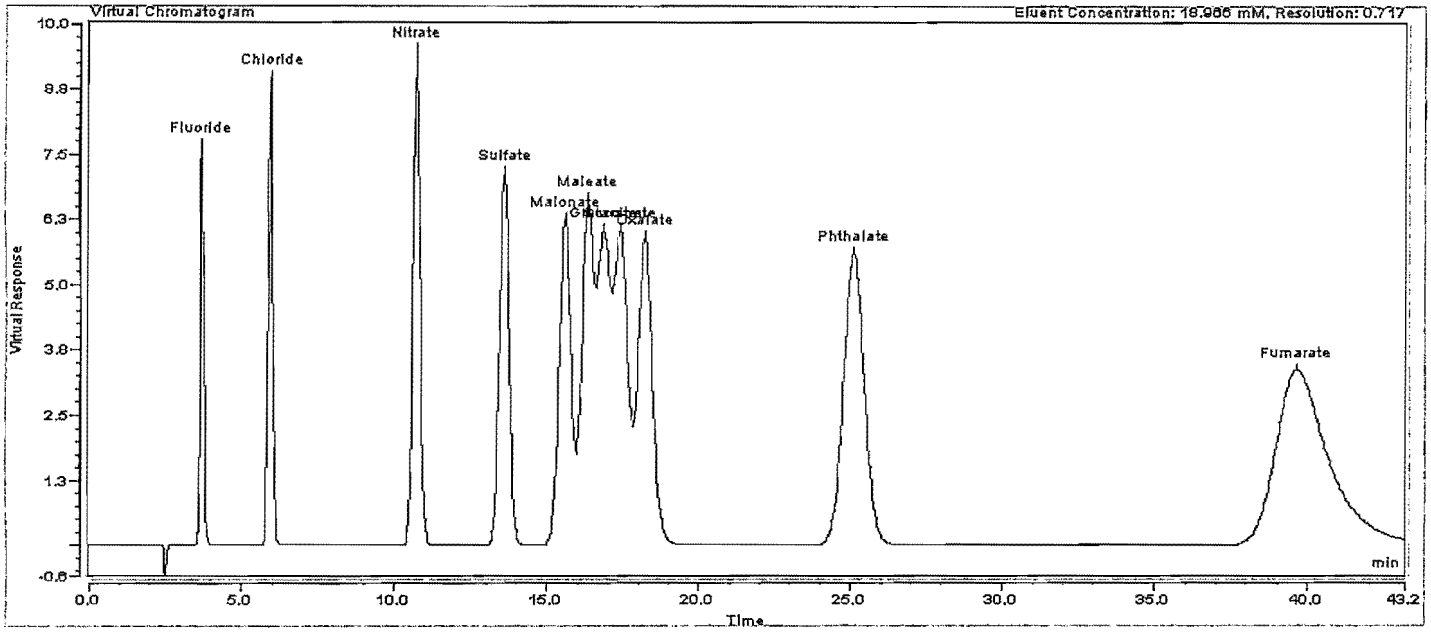
Chromatogram A.8: AS 18 (4x250mm) at 23°C, realistic scenario, gradient



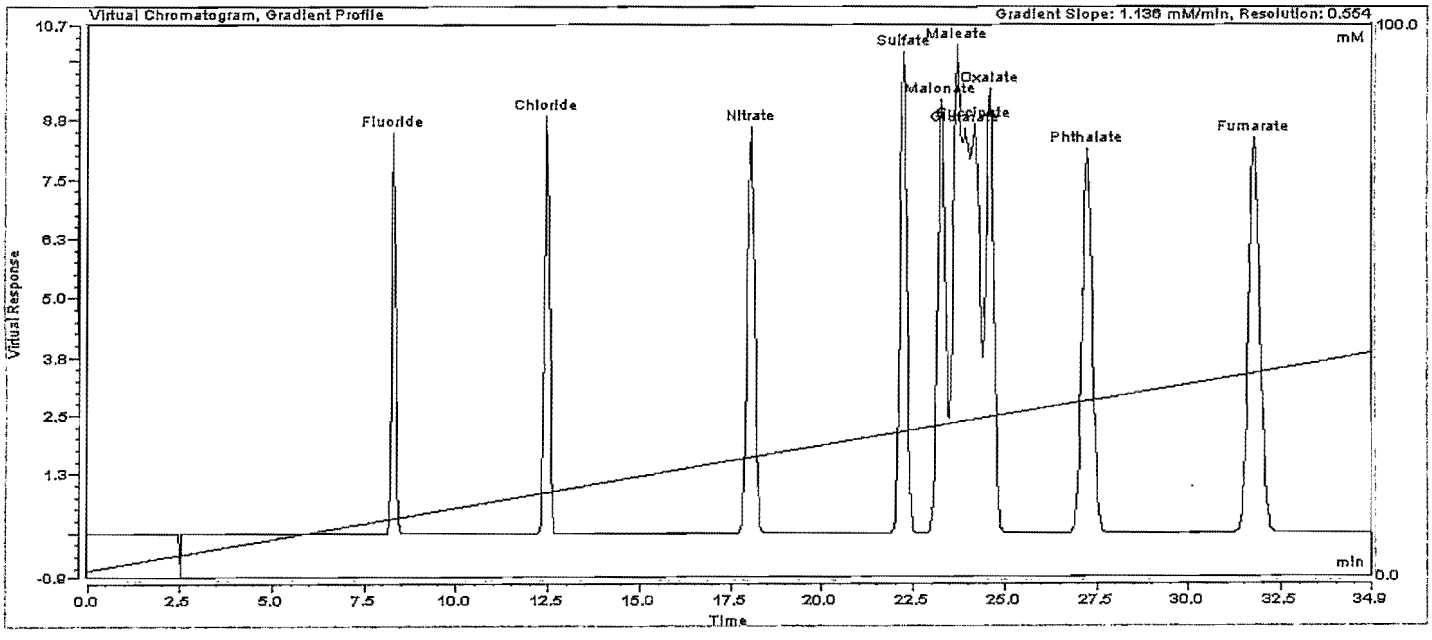
Chromatogram A.9: AS 19 (4x250mm) at 23°C, ideal scenario, isocratic



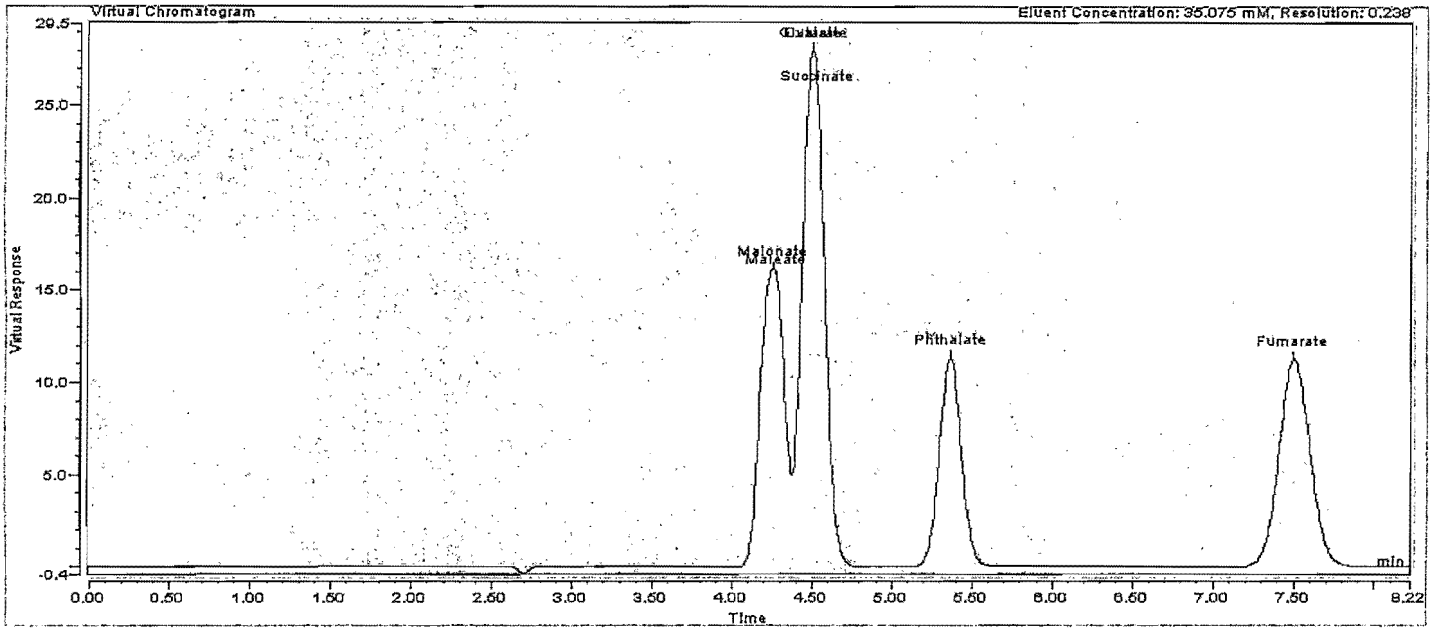
Chromatogram A.10: AS 19 (4x250mm) at 23°C, ideal scenario, gradient



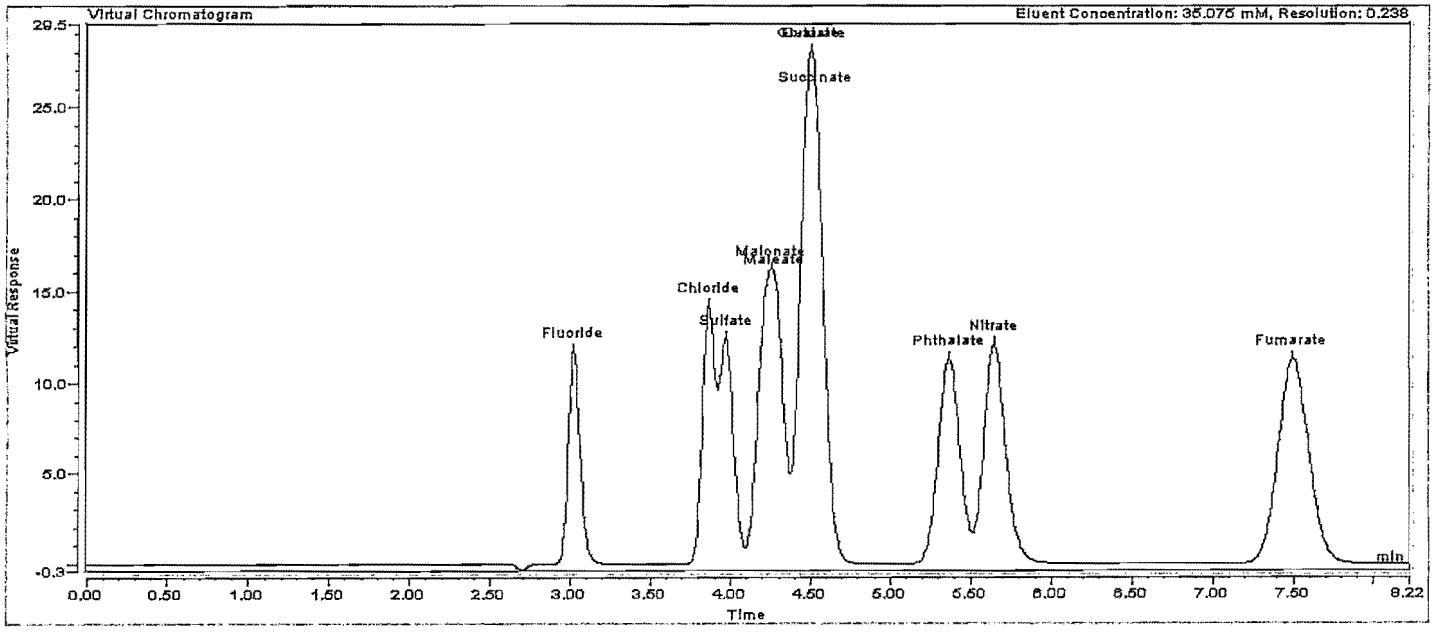
Chromatogram A.11: AS 19 (4x250mm) at 23°C, realistic scenario, isocratic



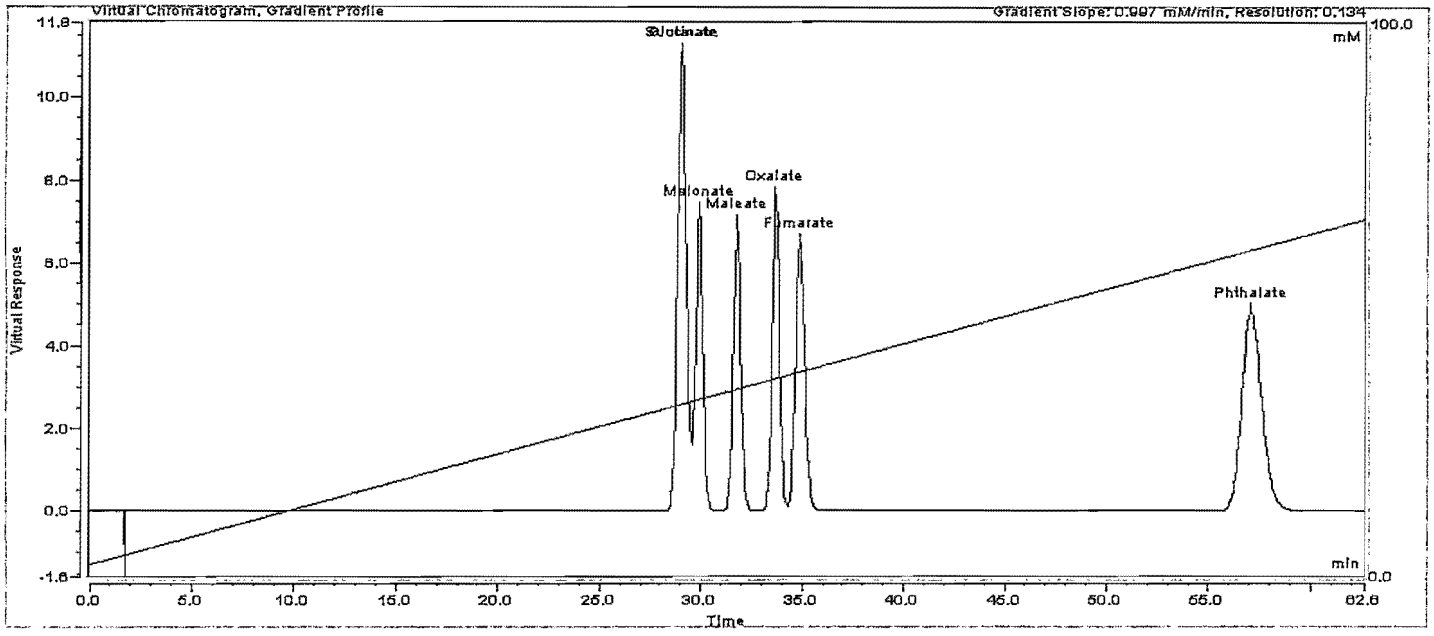
Chromatogram A.12: AS 19 (4x250mm) at 23°C, realistic scenario, gradient



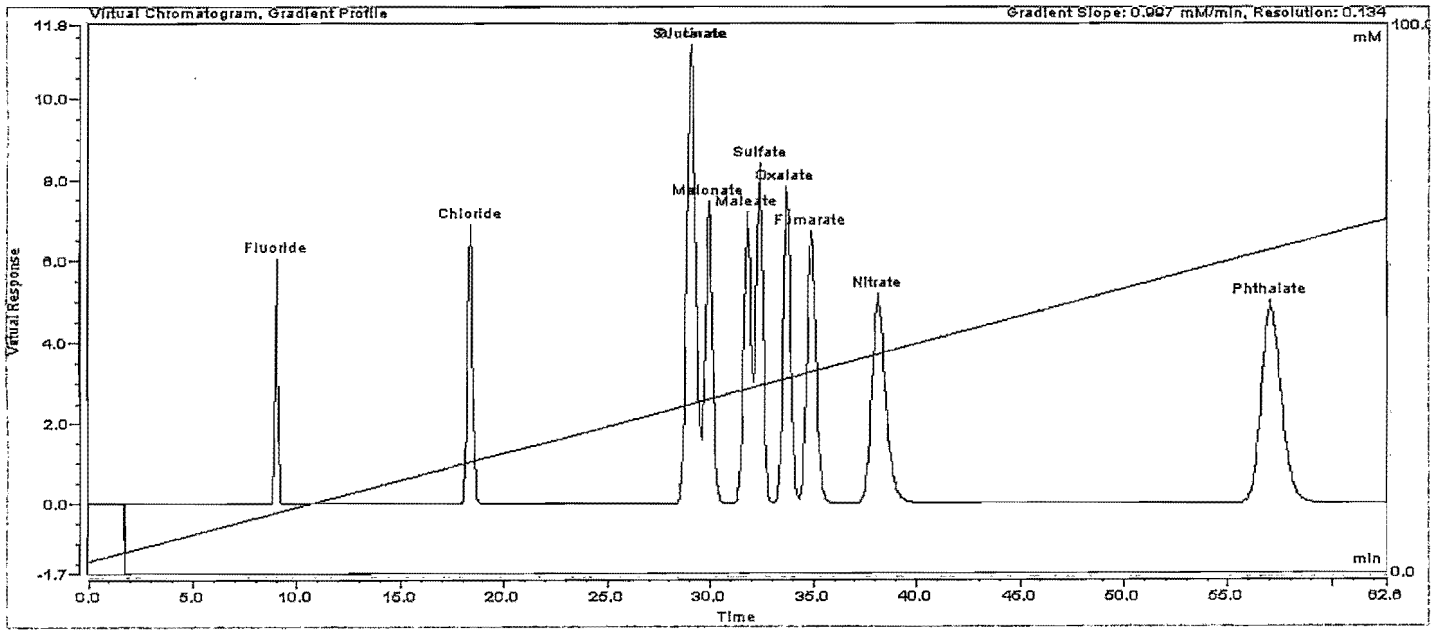
Chromatogram A.13: AS 20 (4x250mm) at 23°C, ideal scenario, isocratic



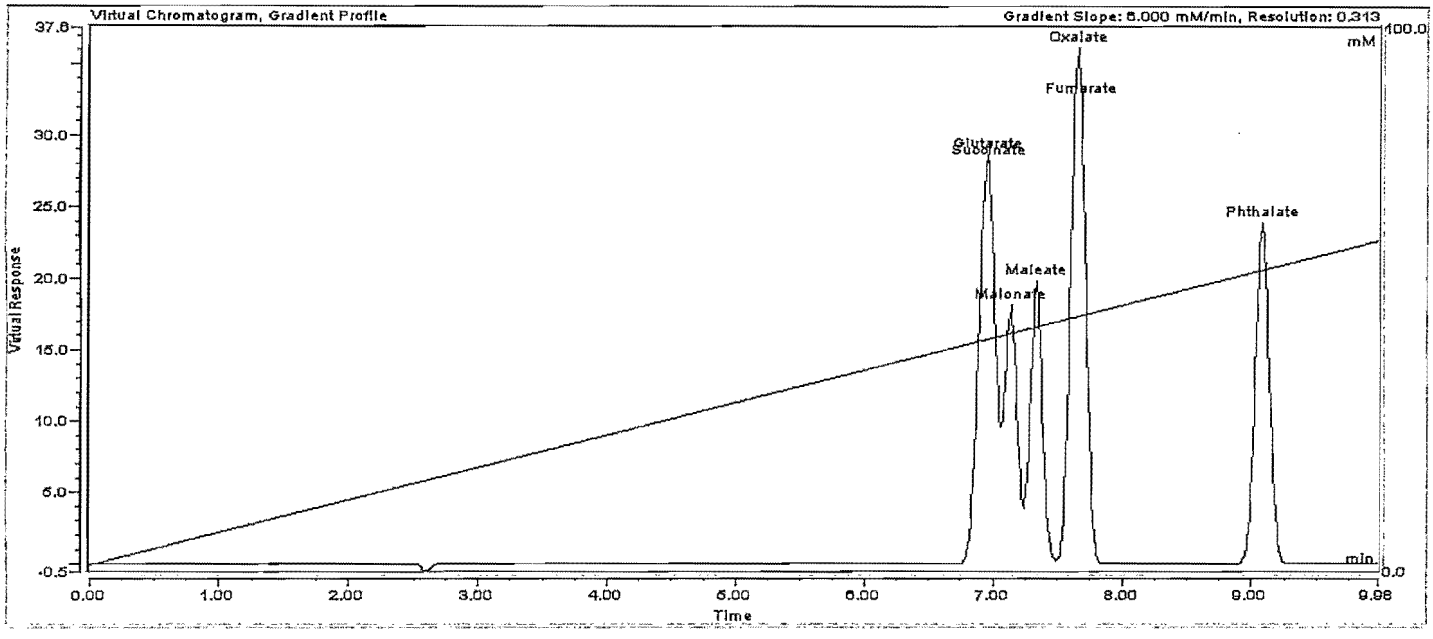
Chromatogram A.14: AS 20 (4x250mm) at 23°C, realistic scenario, isocratic



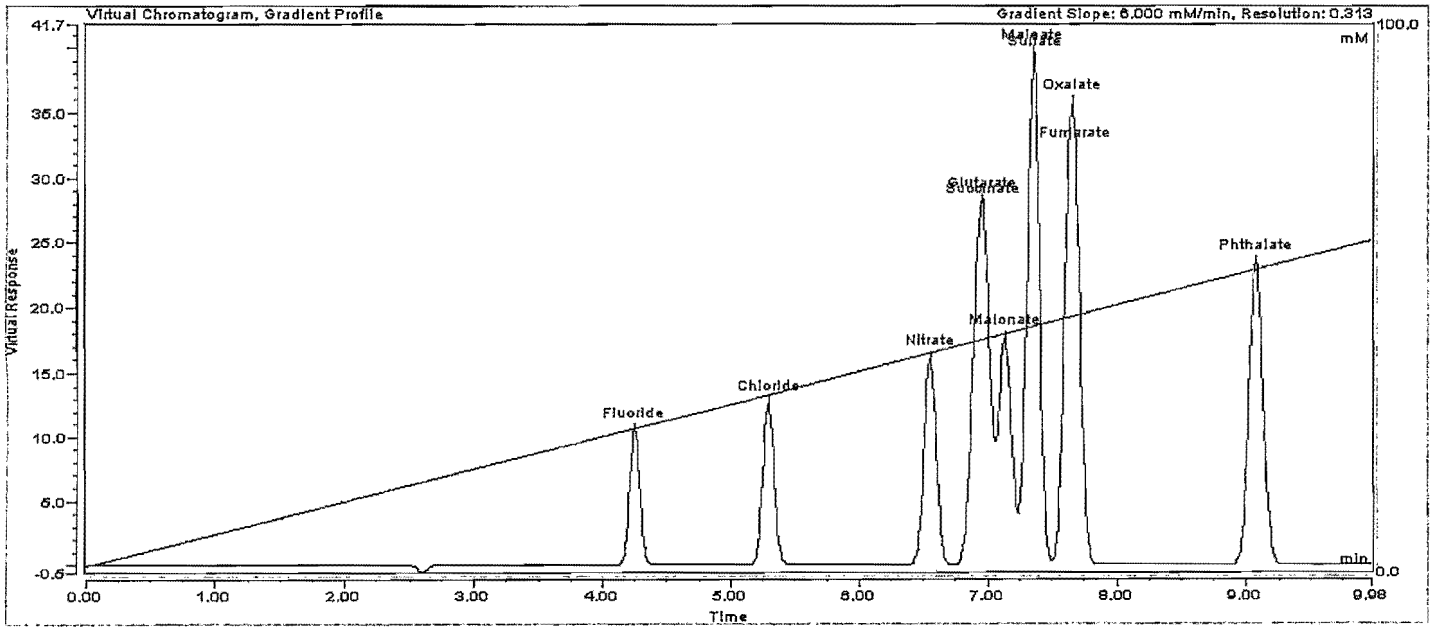
Chromatogram A.15: AS 15 (4x250mm) at 23°C, ideal scenario, gradient



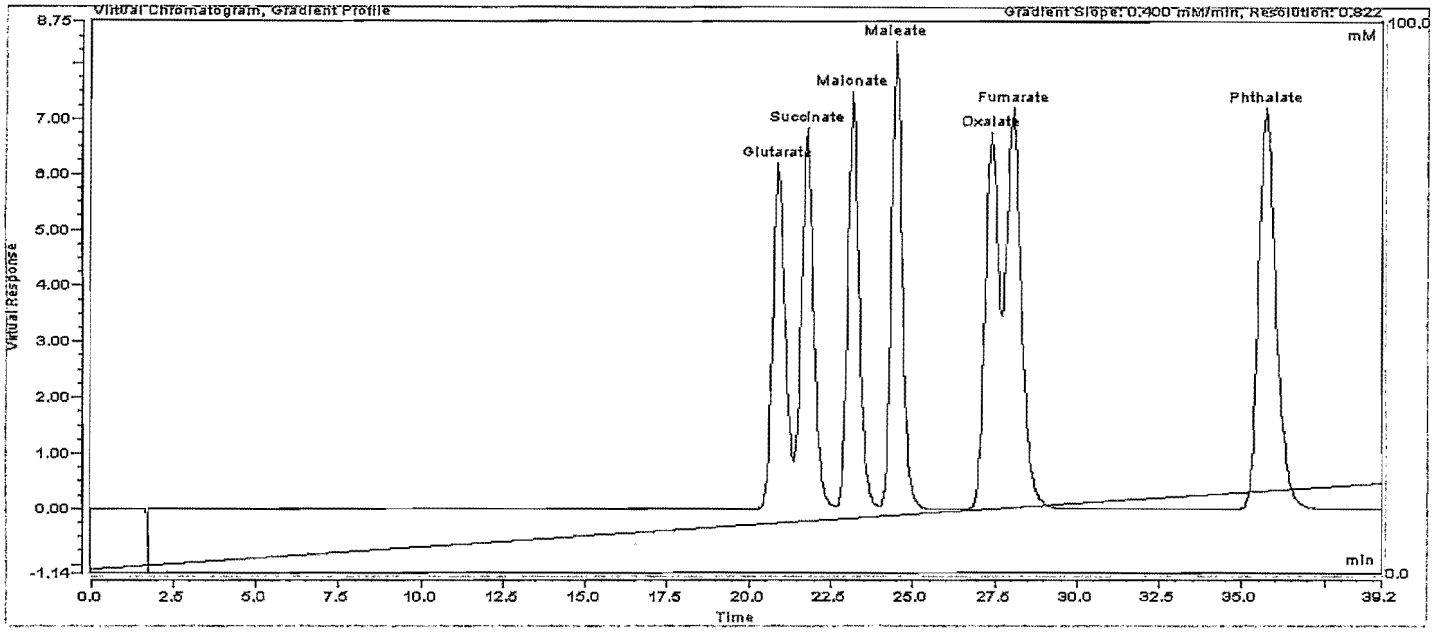
Chromatogram A.16: AS 15 (4x250mm) at 23°C, realistic scenario, gradient



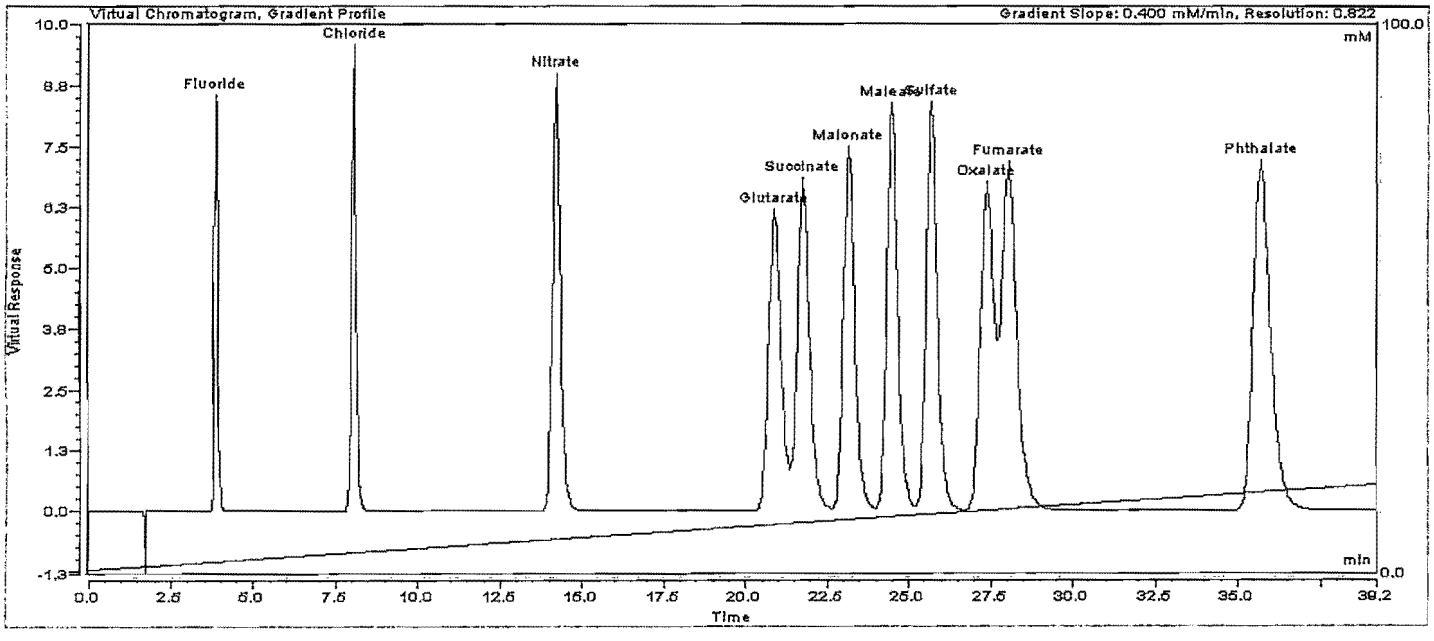
Chromatogram A.17: AS 16 (4x250mm) at 23°C, ideal scenario, gradient



Chromatogram A.18: AS 16 (4x250mm) at 23°C, realistic scenario, gradient



Chromatogram A.19: AS 17 (4x250mm) at 23°C, ideal scenario, gradient



Chromatogram A.20: AS 17 (4x250mm) at 23°C, realistic scenario, gradient

APPENDIX B:
TEMPERATURE OPTIMIZATION

Chromatogram B.1: AS 18 (2x250mm) at 23°C, ideal scenario, isocratic

See Appendix A, chromatogram A.1

Chromatogram B.2: AS 18 (2x250mm) at 23°C, ideal scenario, gradient

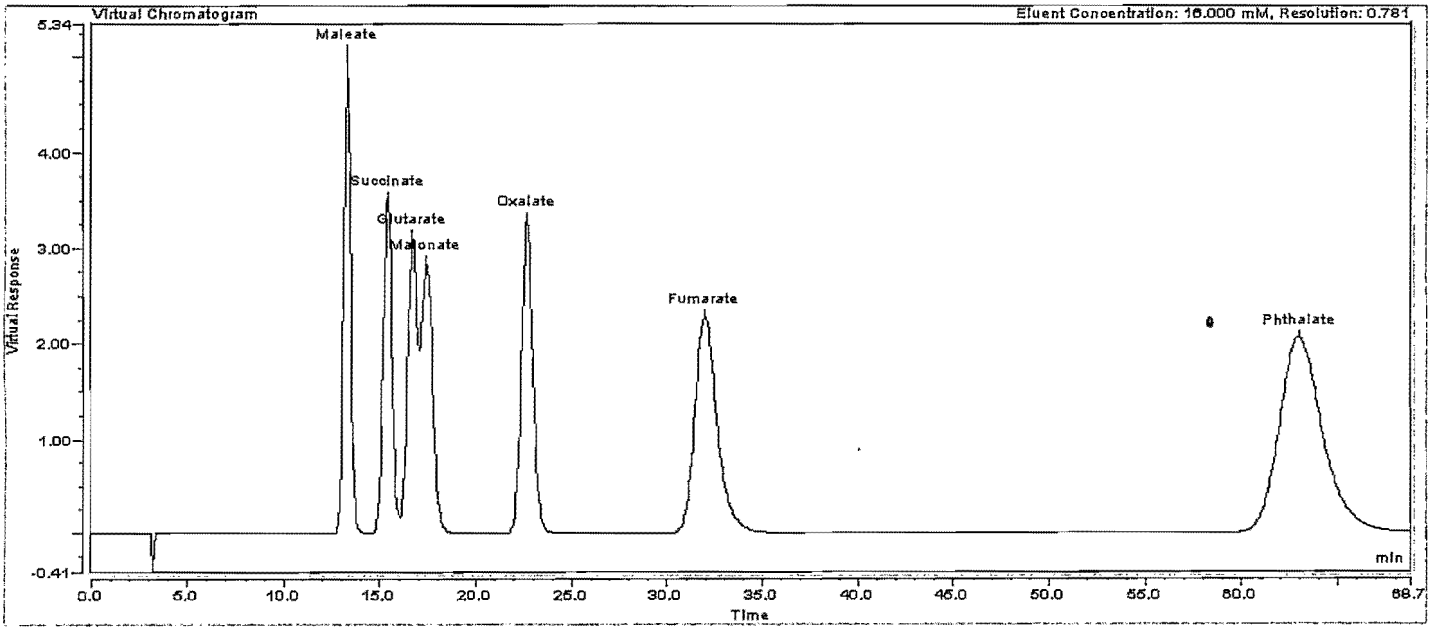
See Appendix A, chromatogram A.2

Chromatogram B.3: AS 18 (2x250mm) at 23°C, realistic scenario, isocratic

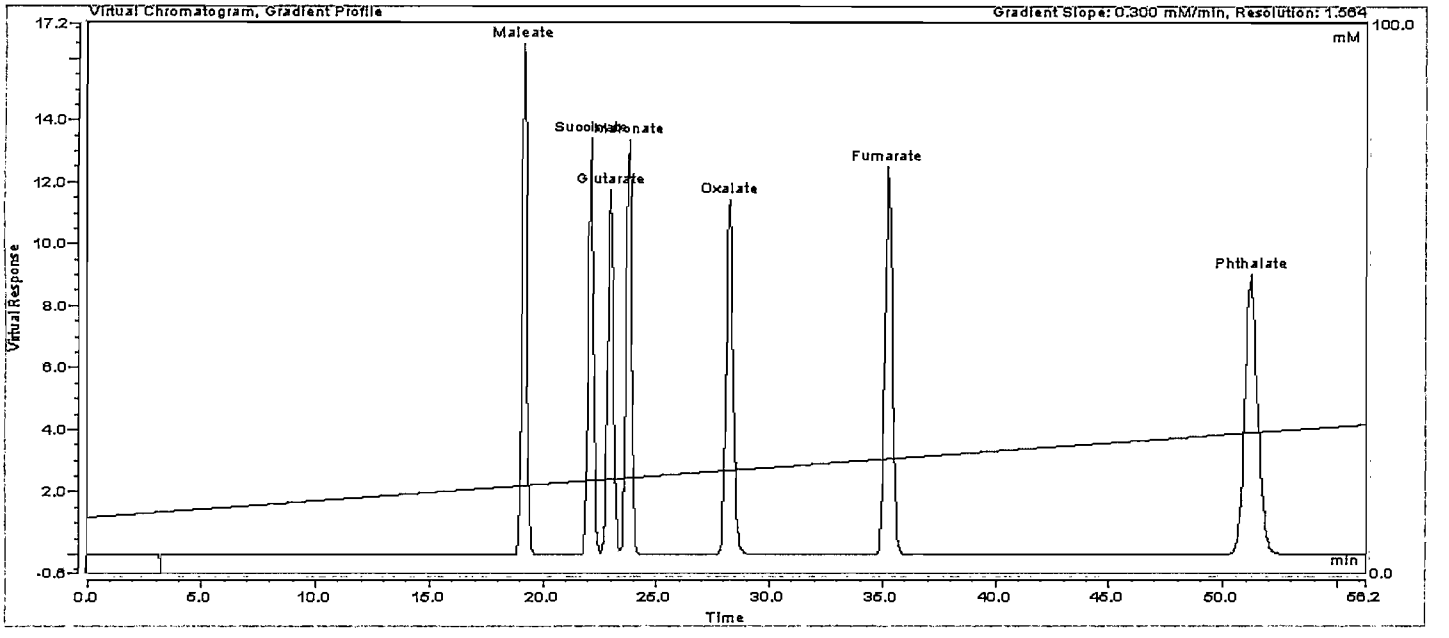
See Appendix A, chromatogram A.3

Chromatogram B.4: AS 18 (2x250mm) at 23°C, realistic scenario, gradient

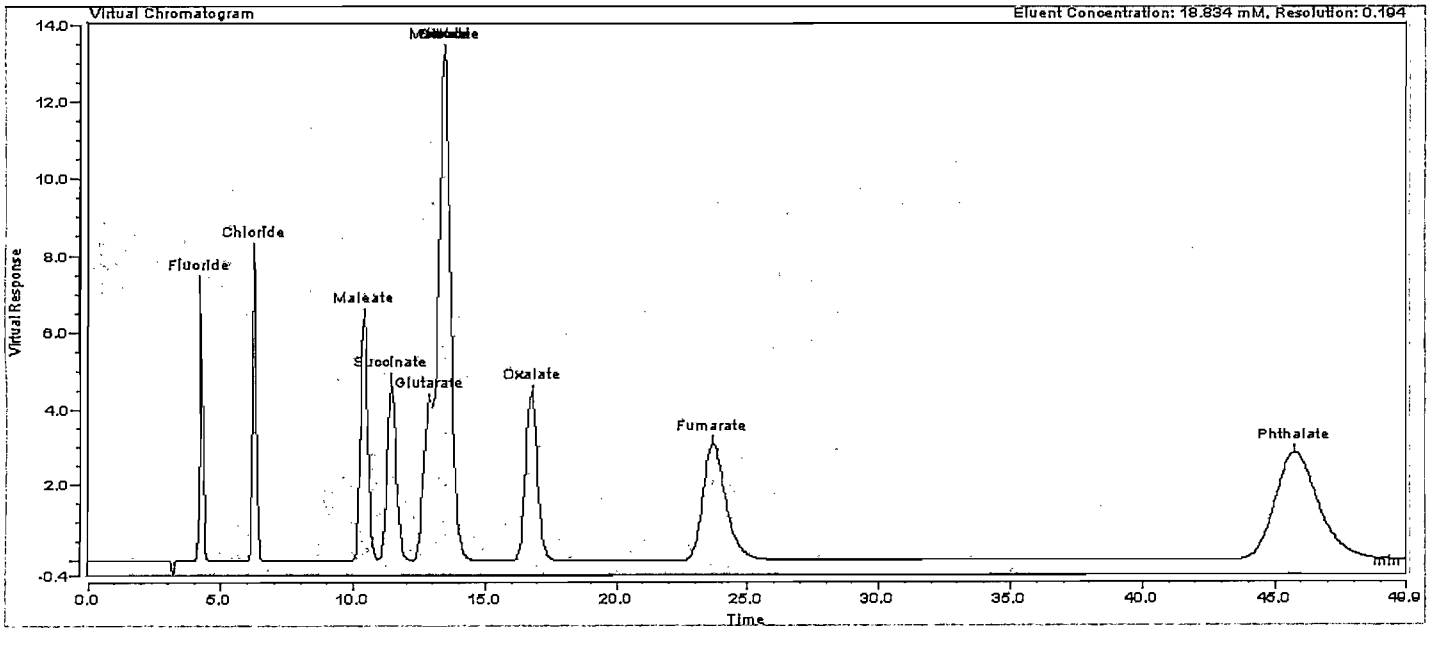
See Appendix A, chromatogram A.4



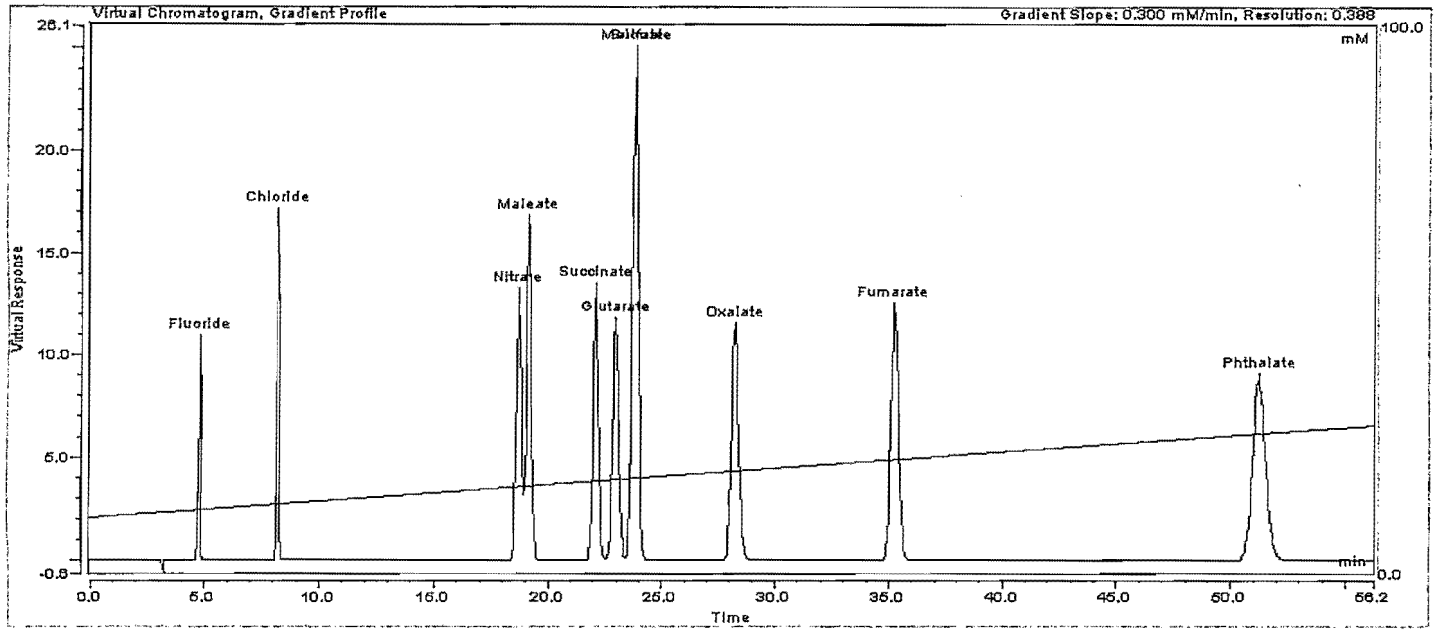
Chromatogram B.5: AS 18 (2x250mm) at 30°C, ideal scenario, isocratic



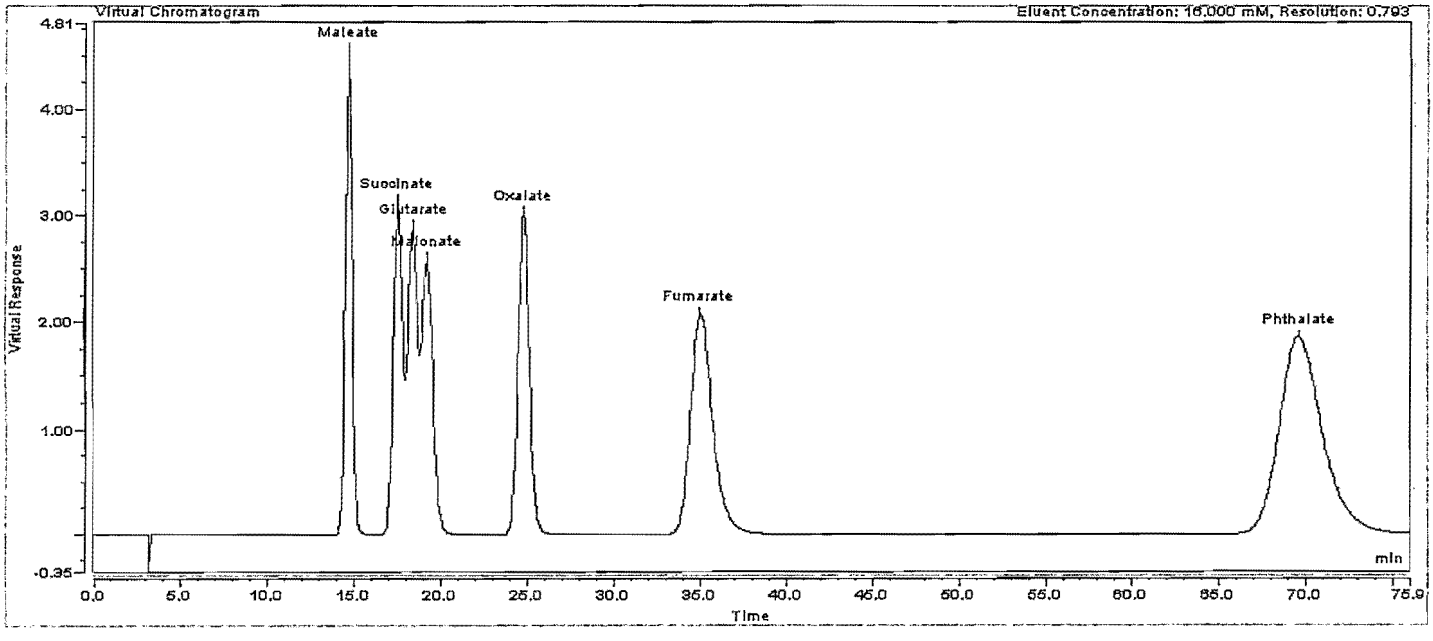
Chromatogram B.6: AS 18 (2x250mm) at 30°C, ideal scenario, gradient



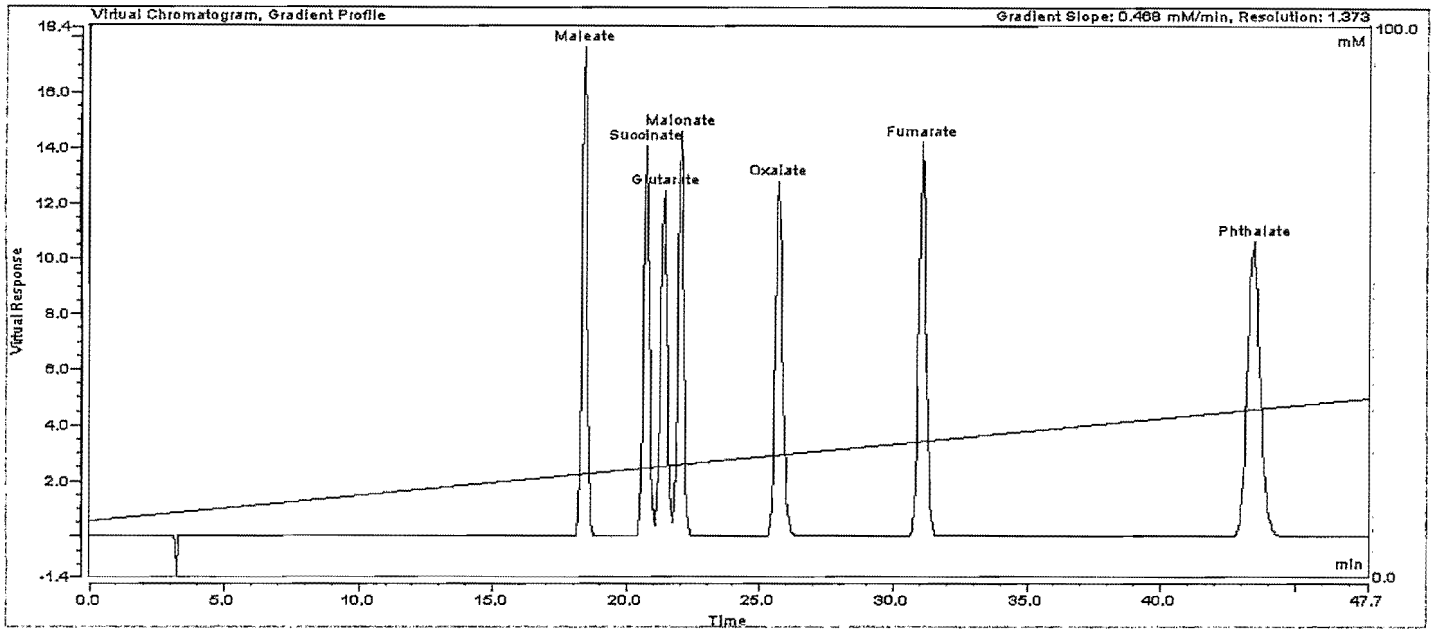
Chromatogram B.7: AS 18 (2x250mm) at 30°C, realistic scenario, isocratic



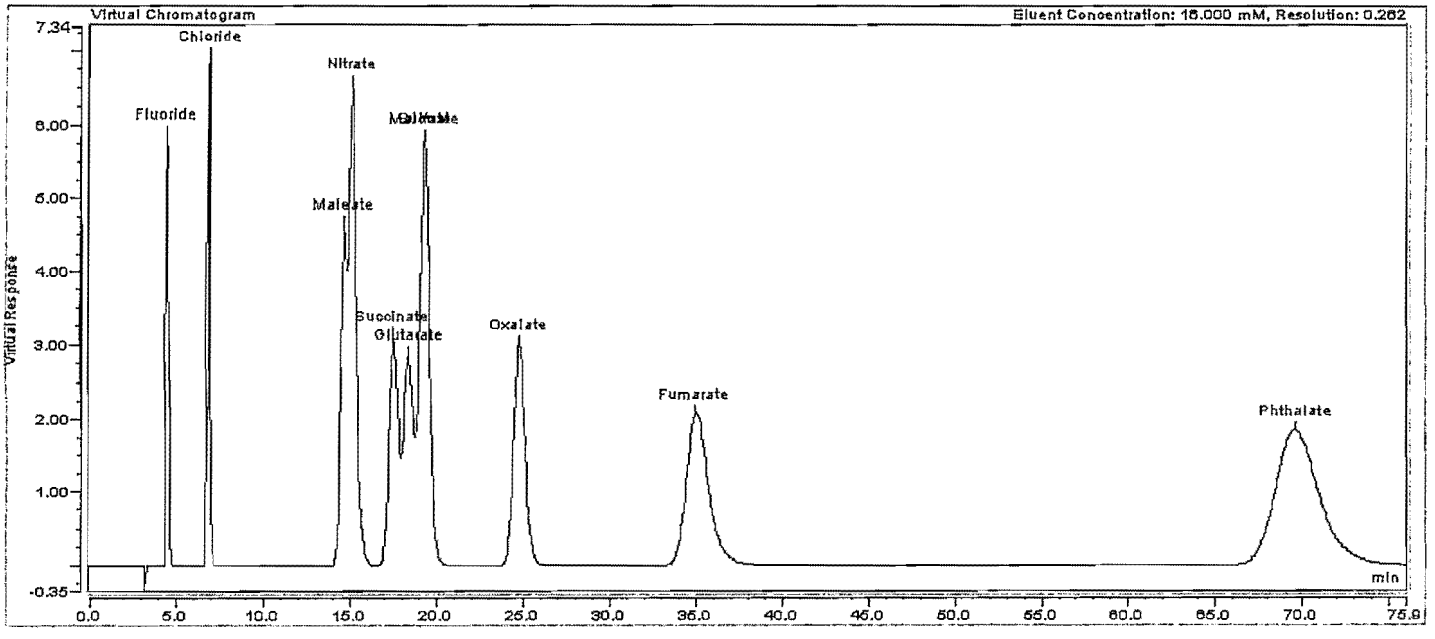
Chromatogram B.8: AS 18 (2x250mm) at 30°C, realistic scenario, gradient



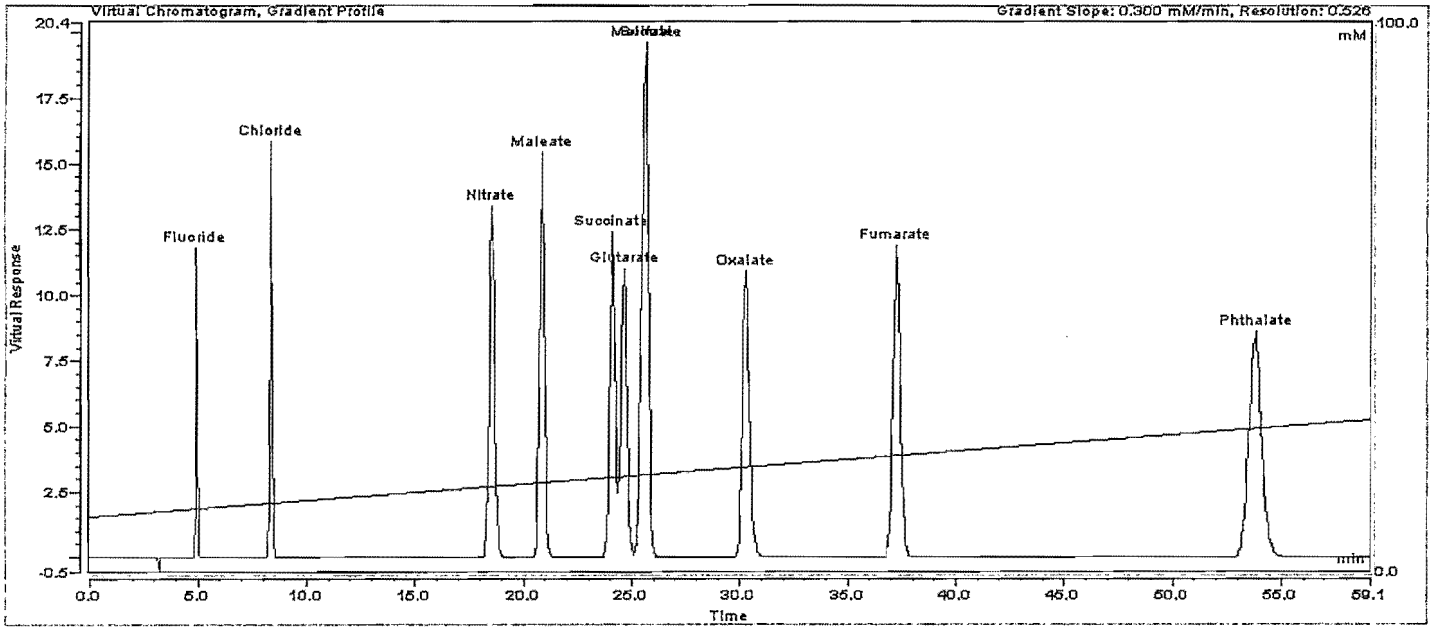
Chromatogram B.9: AS 18 (2x250mm) at 35°C, ideal scenario, isocratic



Chromatogram B.10: AS 18 (2x250mm) at 35°C, ideal scenario, gradient



Chromatogram B.11: AS 18 (2x250mm) at 35°C, realistic scenario, isocratic



Chromatogram B.12: AS 18 (2x250mm) at 35°C, realistic scenario, gradient

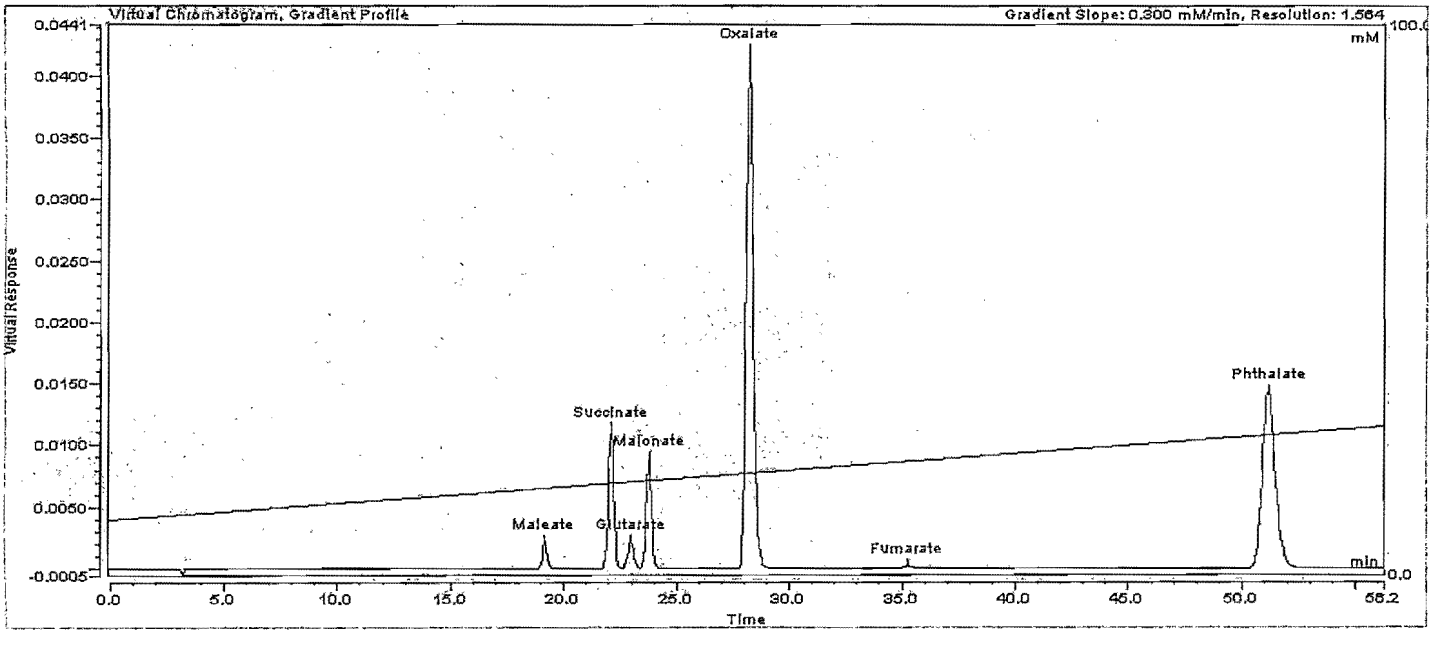
APPENDIX C:
DICARBOYLIC ACID CONCENTRATION OPTIMIZATION

Chromatogram C.1: AS 18 (2x250mm) at 30°C, ideal scenario, gradient

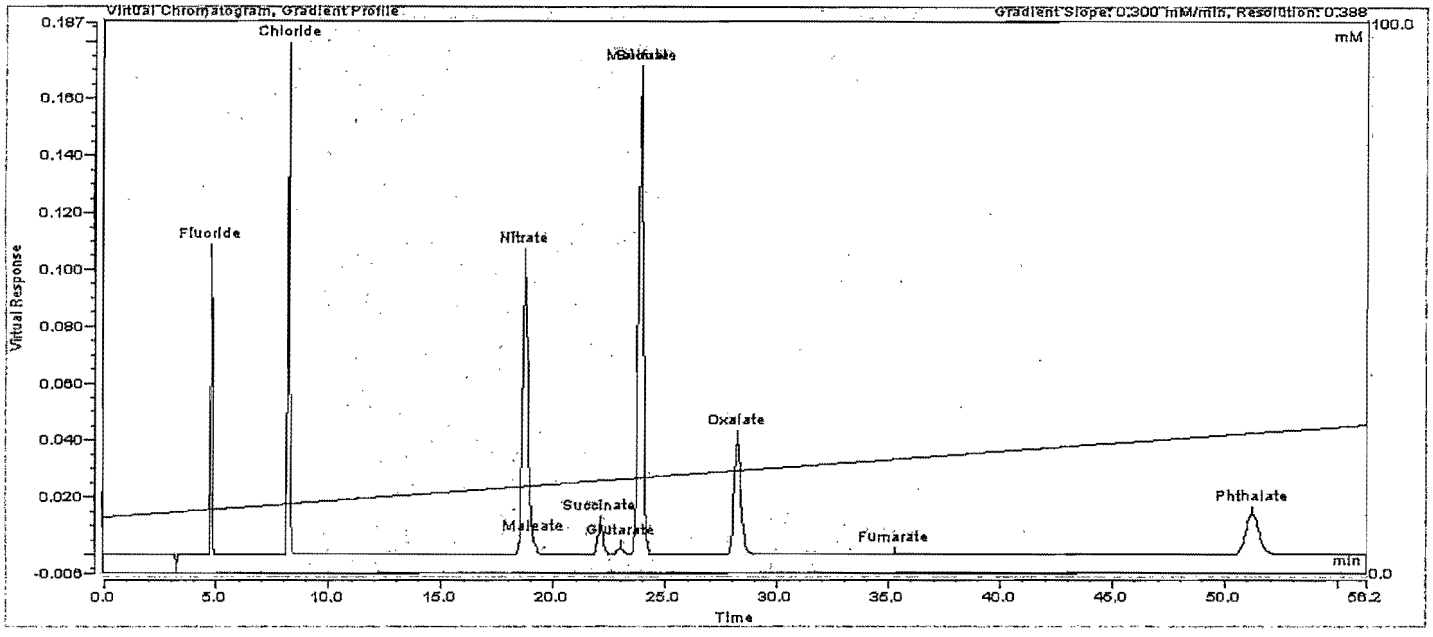
See Appendix B, chromatogram B.6

Chromatogram C.2: AS 18 (2x250mm) at 30°C, realistic scenario, gradient

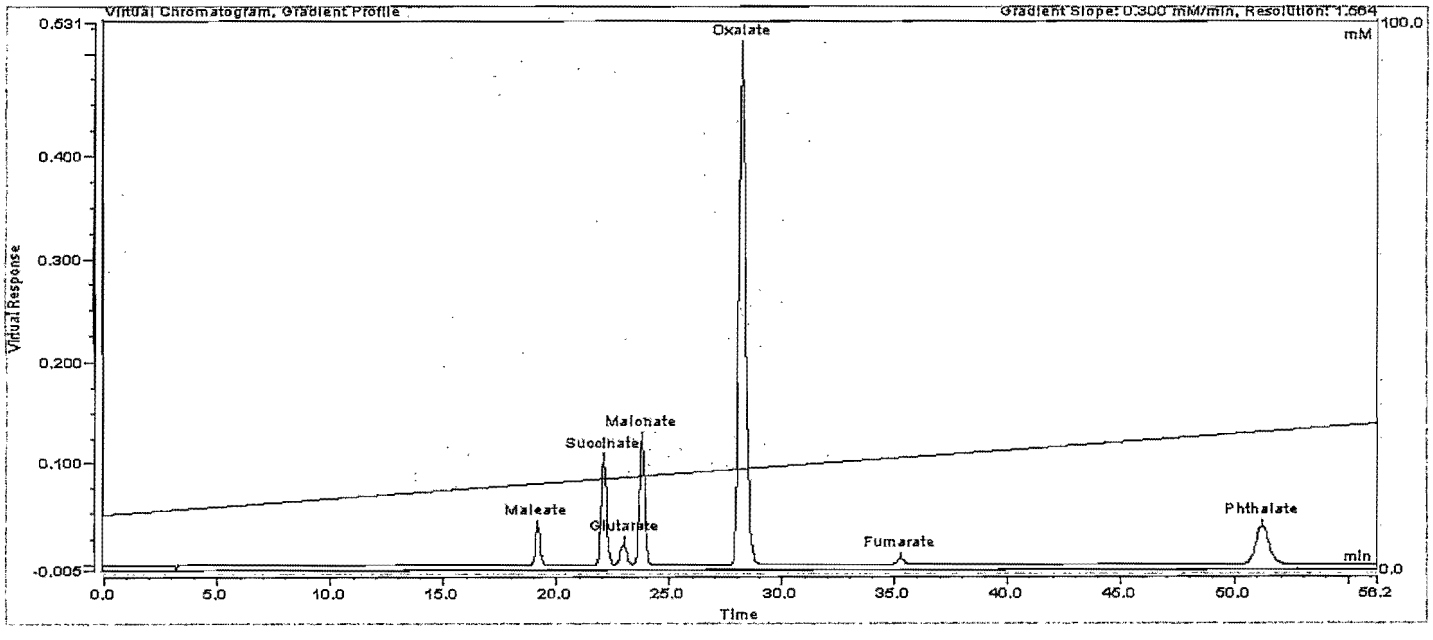
See Appendix B, chromatogram B.8



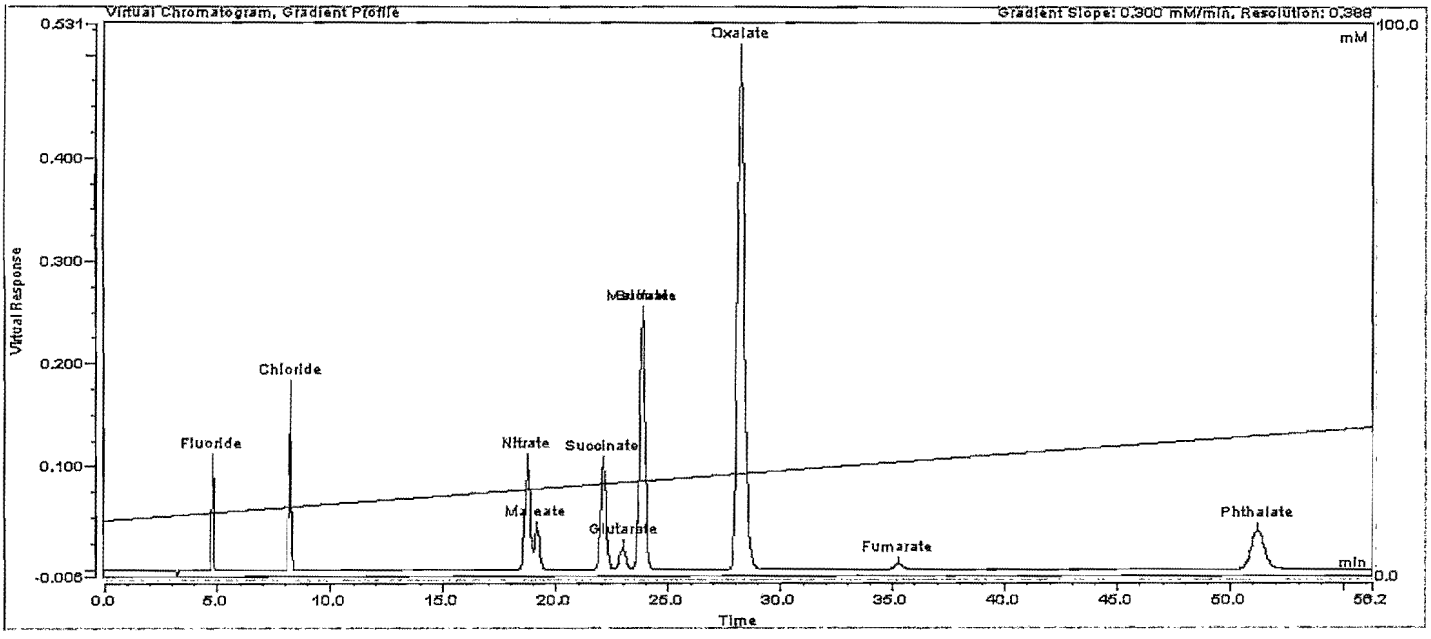
Chromatogram C.3: AS 18 (2x250mm) at 30°C, ideal scenario of low literature concentrations with gradient elution



Chromatogram C.4: AS 18 (2x250mm) at 30°C, realistic scenario of low literature concentrations with gradient elution



Chromatogram C.5: AS 18 (2x250mm) at 30°C, ideal scenario of high literature concentrations with gradient elution



Chromatogram C.6: AS 18 (2x250mm) at 30°C, realistic scenario of high literature concentrations with gradient

C.7 Conversion calculations

Step 1: How the literature converts their GC values to mg or ng/m^3

$$IC\ or\ GC\ values\ (mg/l) \times \frac{1l}{100\ ml} \times 30\ ml\ extraction\ water = mg\ species\ on\ the\ filter$$

Step 2:

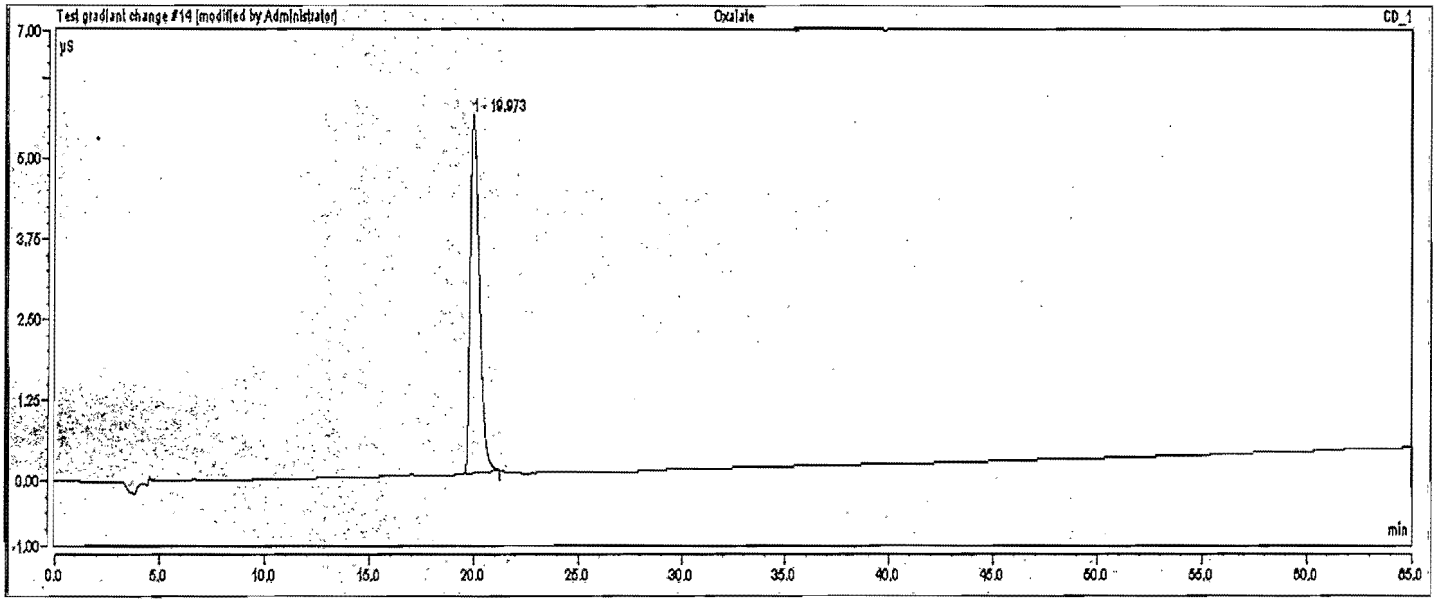
$$\frac{mg\ \ species\ \ on\ \ filter}{m^3\ \ Air\ \ volume} = mg\ /\ m^3\ species\ in\ the\ air$$

Air volume: (24h, 5l/min) = 24 x 60 minutes x 5 l/minutes = 7.2 m^3

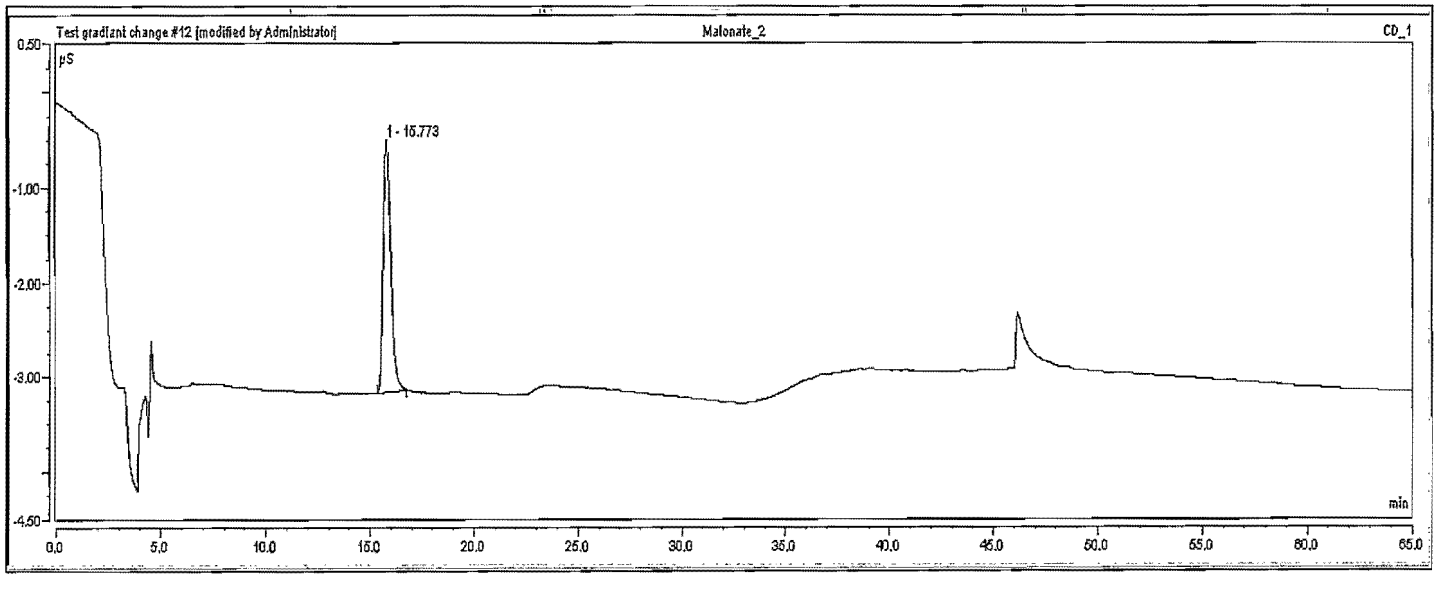
Step 3: Converted PM 2.5 GC concentration values to expected IC concentration values of the study undertaken by Ho et al., (2006) in Hong Kong

	GC values		IC values	
	Low (ng/m^3)	**High (ng/m^3)**	**Low (mg/l)**	**High (mg/l)**
C_2	63.8	767	0.015312	0.18408
C_3	10.5	145	0.00252	0.0348
C_4	13.1	121	0.003144	0.02904
C_5	2.82	28.1	0.006768	0.006744
Ph	40.1	105	0.009624	0.0252
M	2.21	37.2	0.0005304	0.008928
F	0.29	8.66	0.0000696	0.0020784

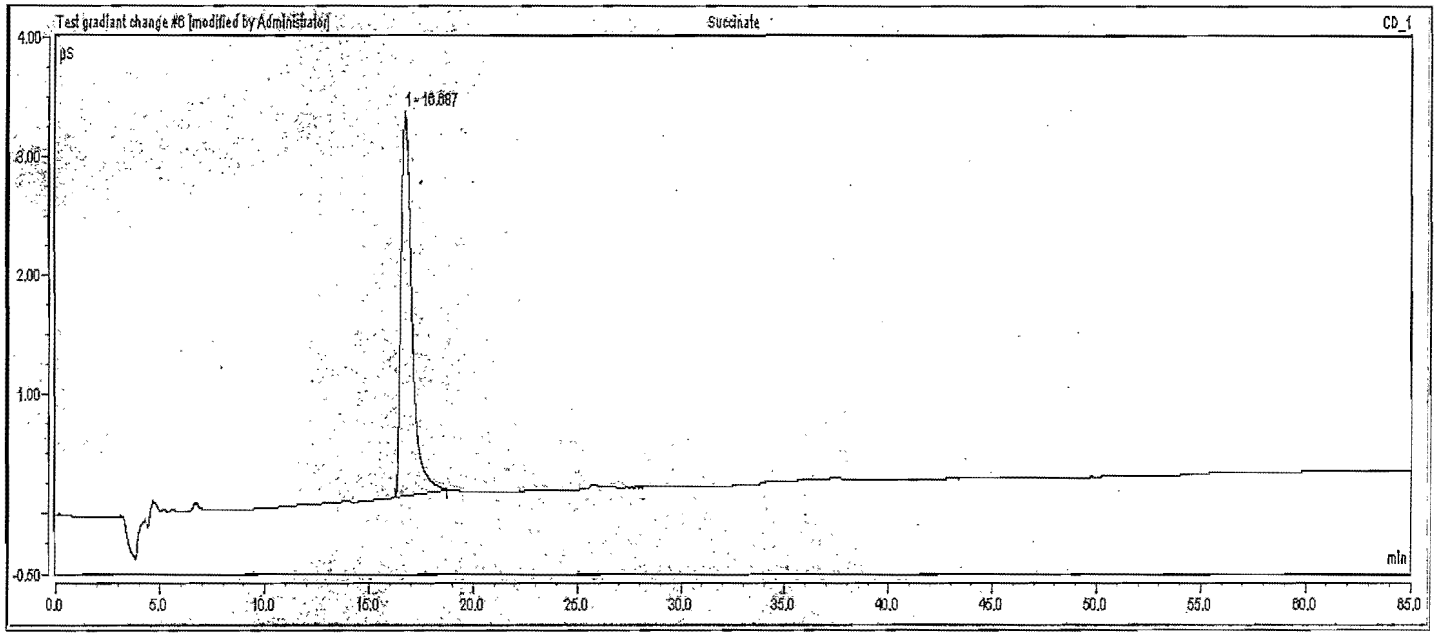
APPENDIX D:
DICARBOXYLIC ACID AND INORGANIC ION STANDARDS



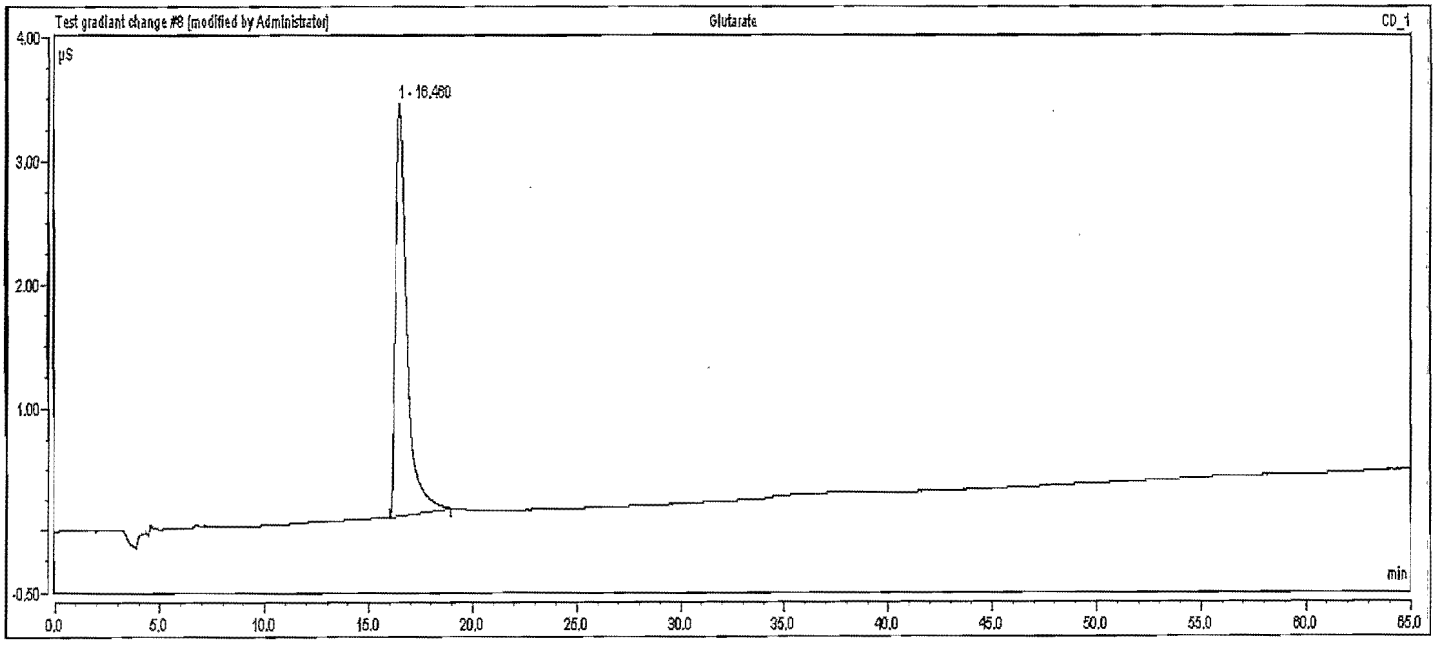
Chromatogram D.1: Oxalic acid (C_2)



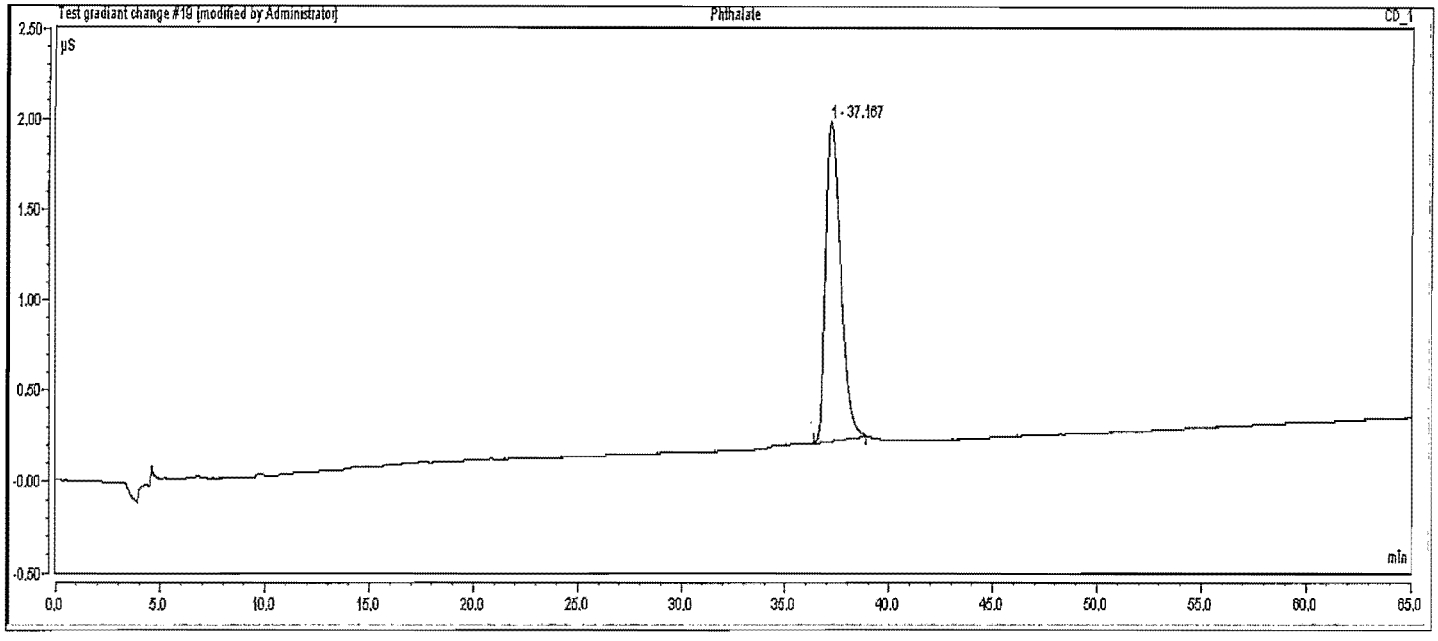
Chromatogram D.2: Malonic acid (C_3)



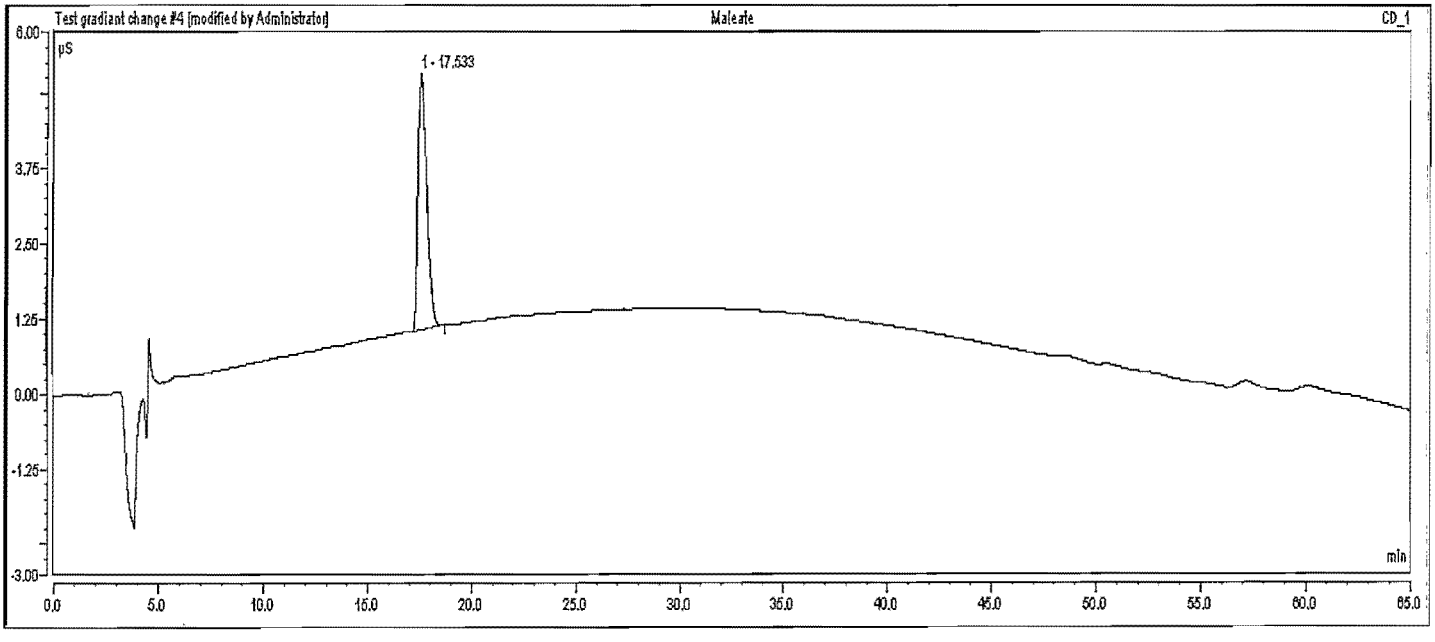
Chromatogram D.3: Succinic acid (C_4)



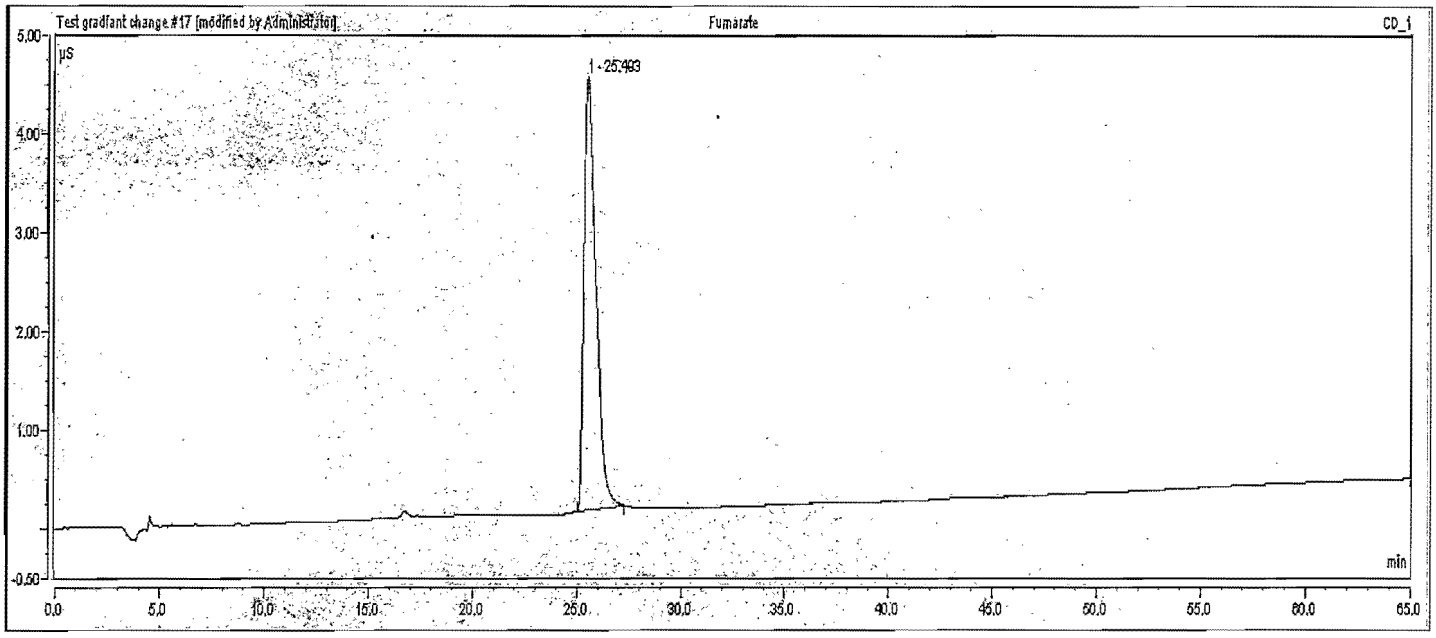
Chromatogram D.4: Glutaric acid (C_5)



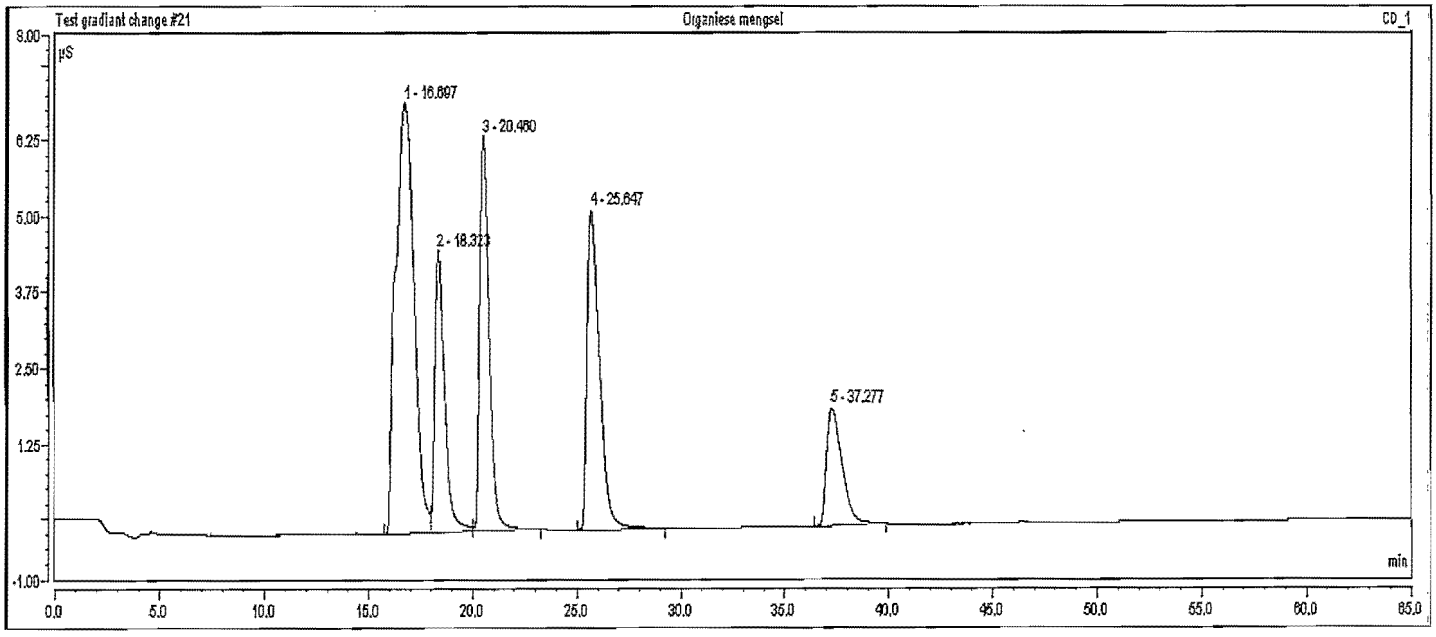
Chromatogram D.5: Phthalic acid (Ph)



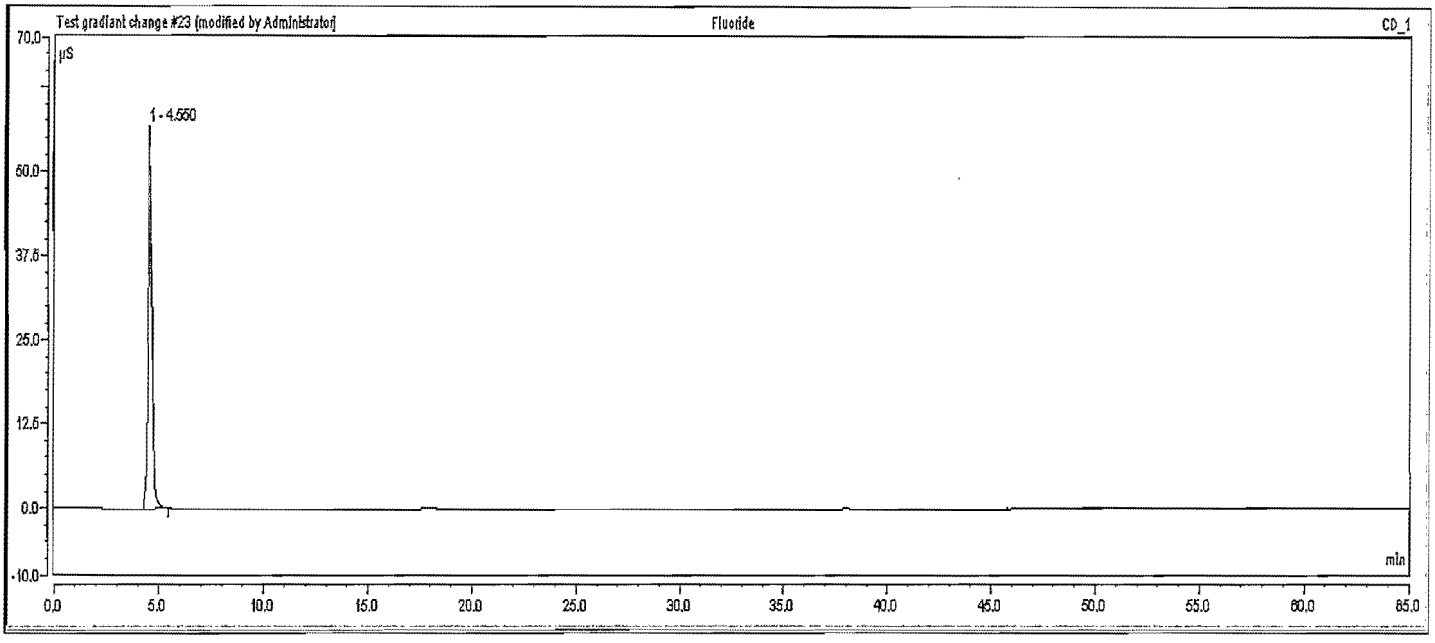
Chromatogram D.6: Maleate (M)



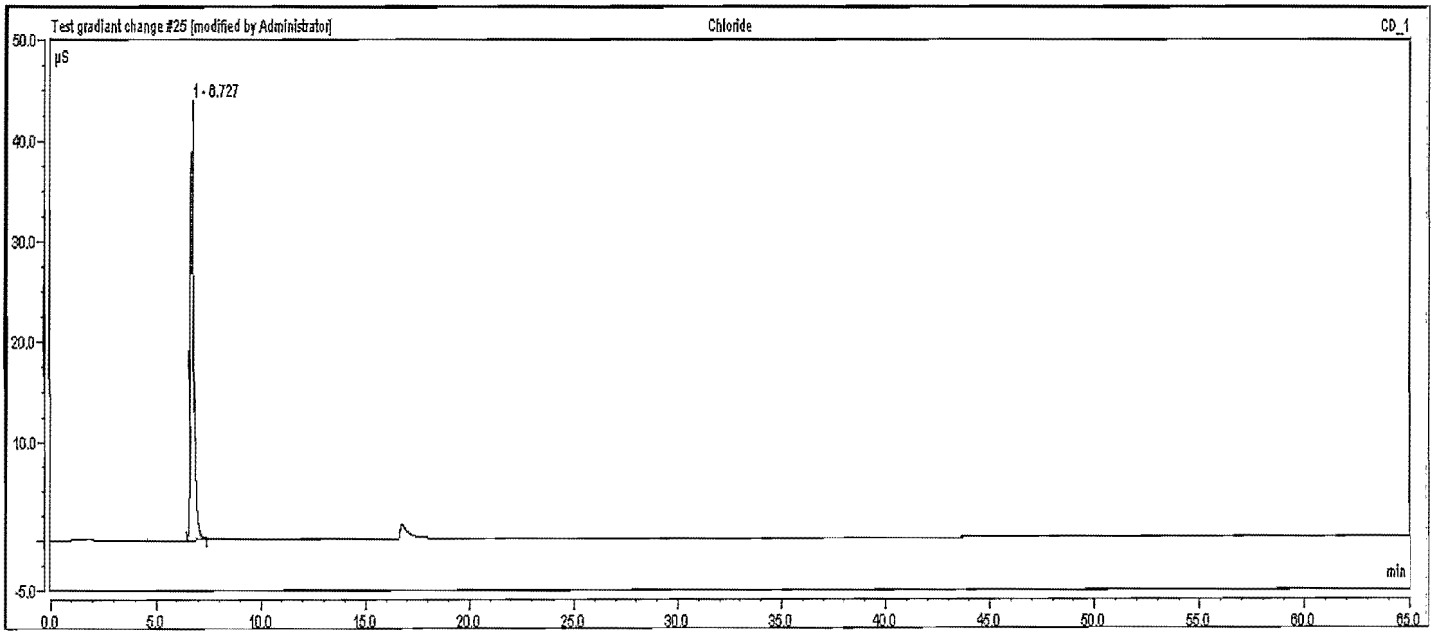
Chromatogram D.7: Fumaric acid (F)



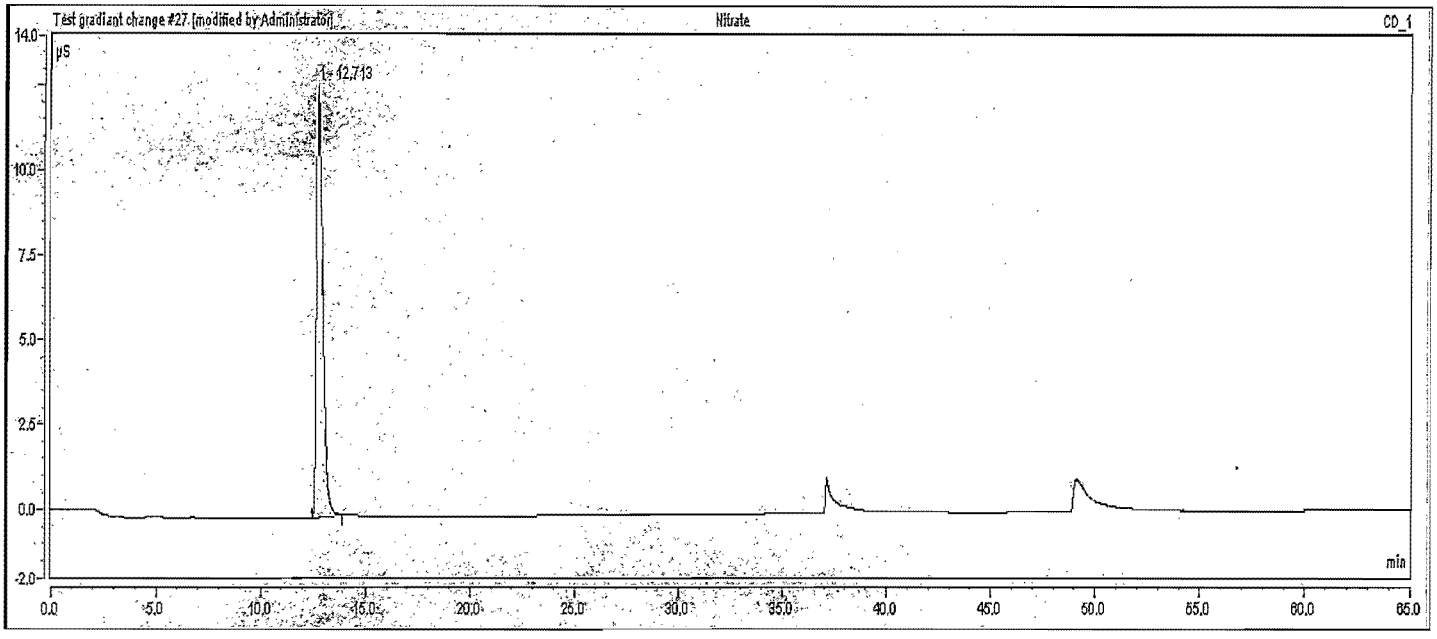
Chromatogram D.8: Organic solution containing all 7 dicarboxylic acid standards



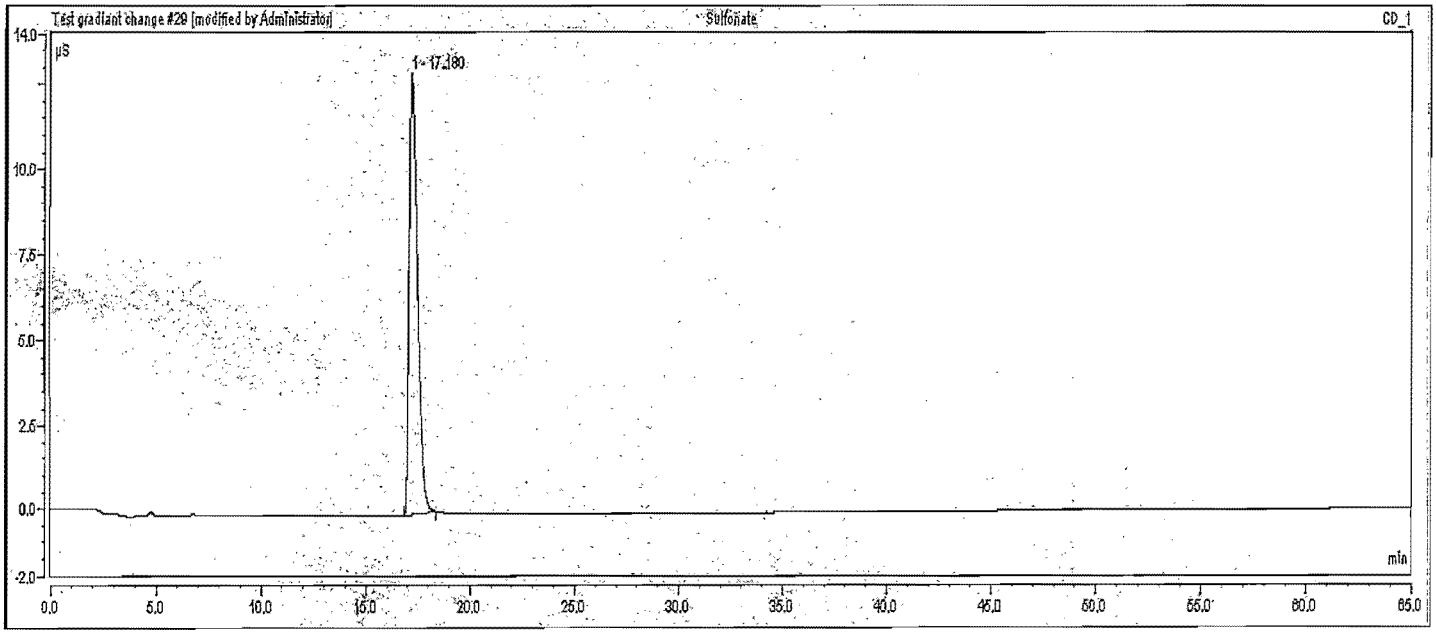
Chromatogram D.9: Fluoride



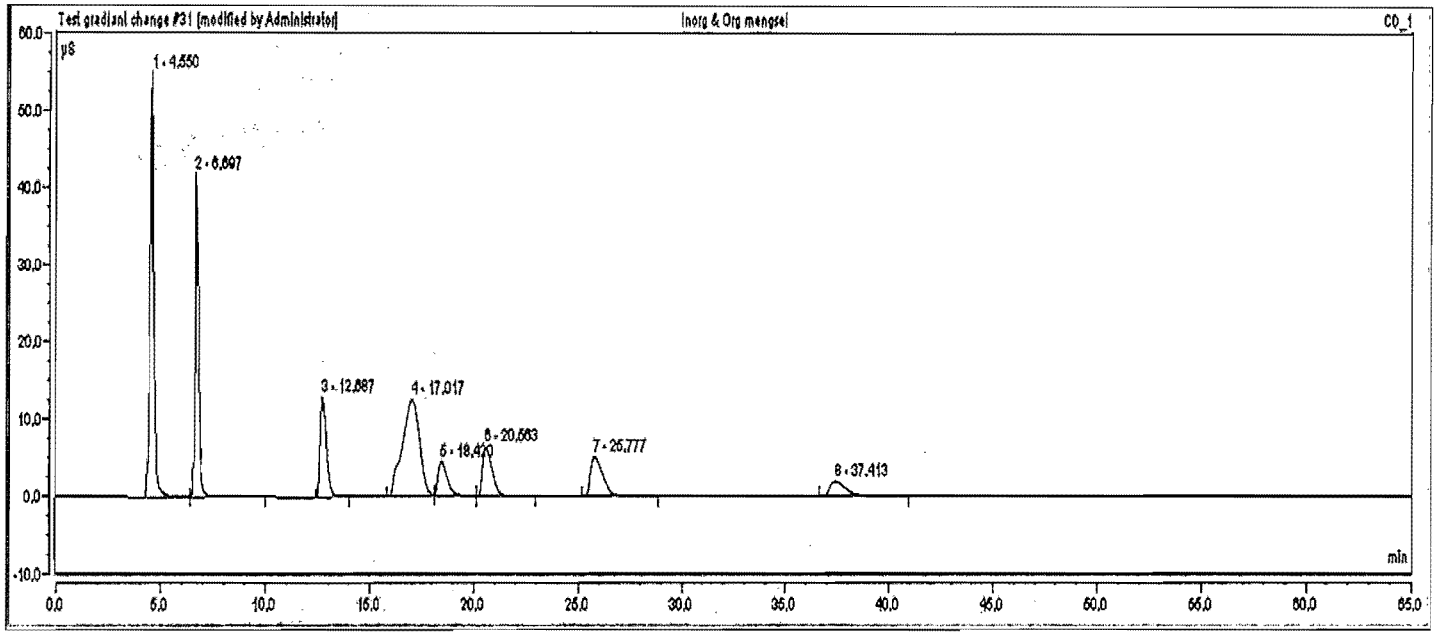
Chromatogram D.10: Chloride



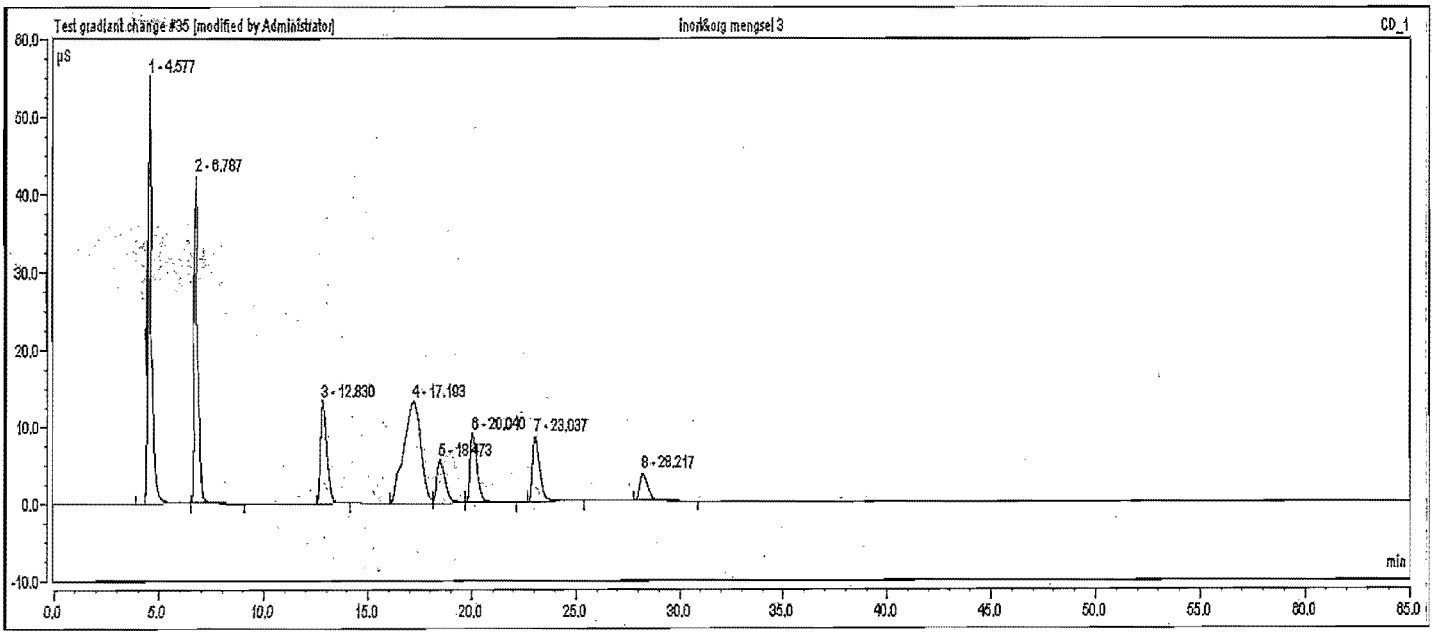
Chromatogram D.11: Nitrate



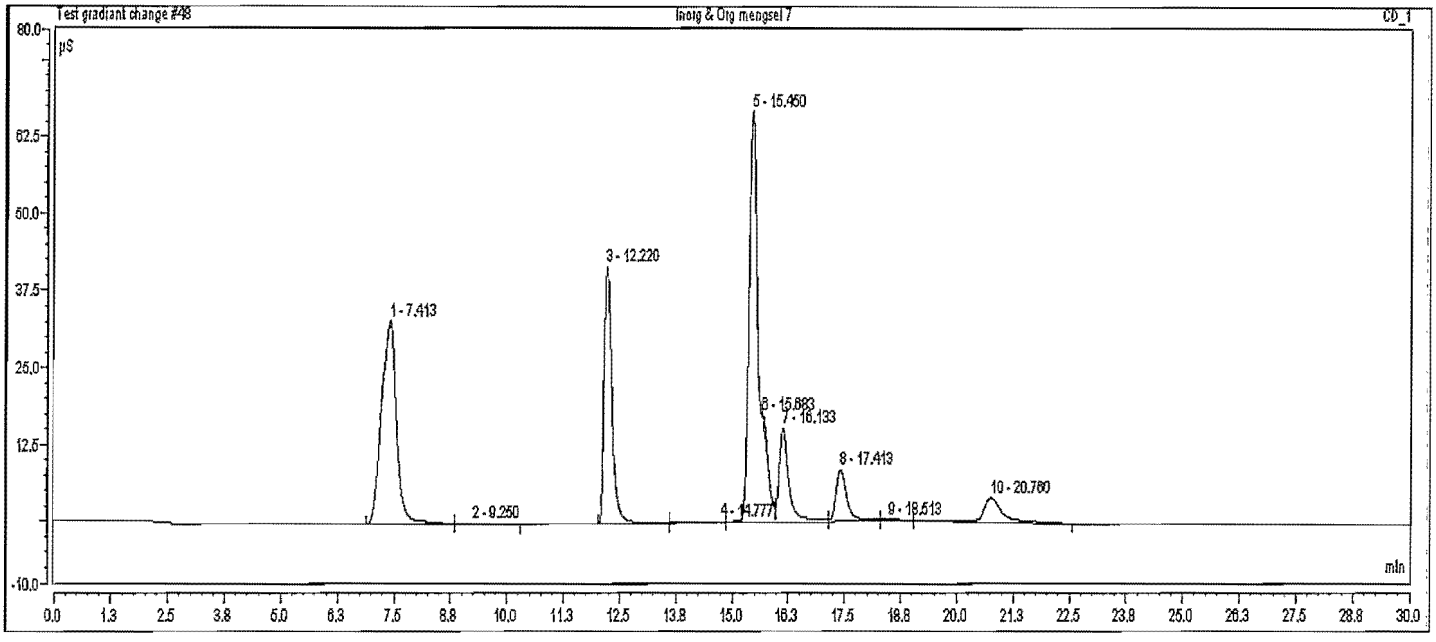
Chromatogram D.12: Sulphate



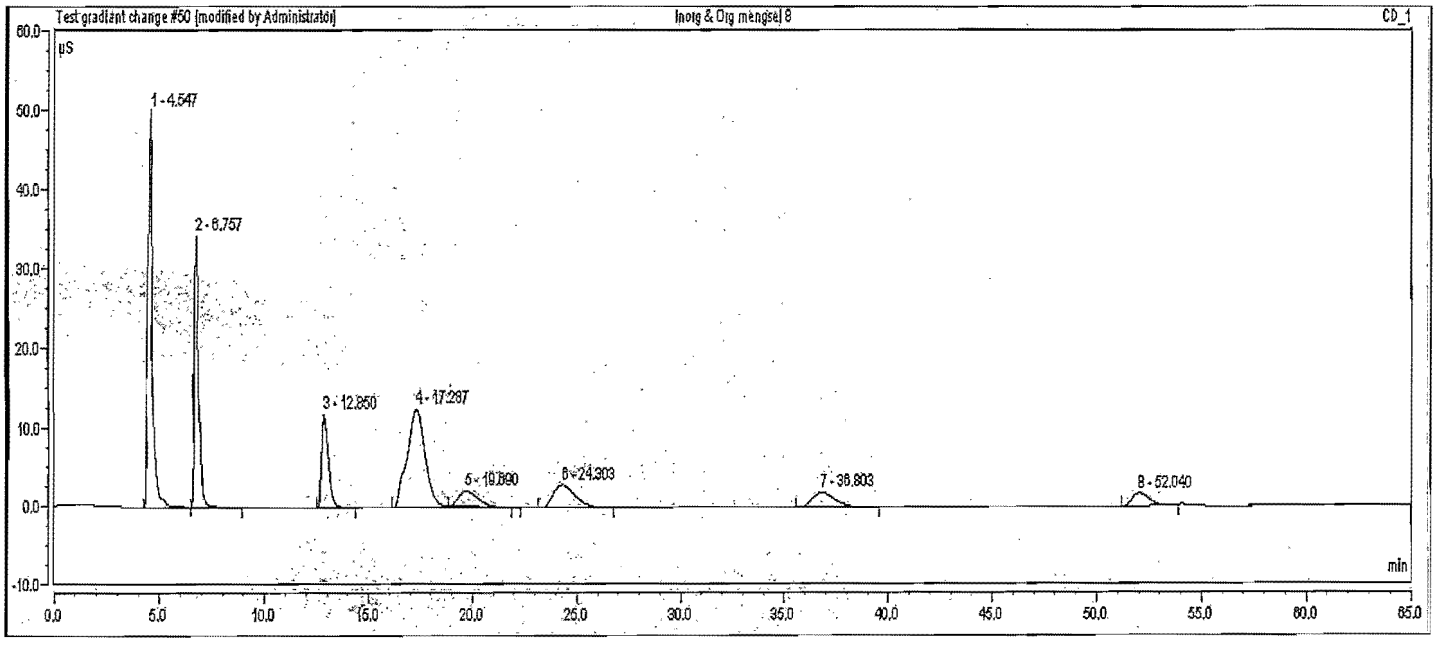
Chromatogram D.13: Standard solution containing all 7 dicarboxylic acids and 4 inorganic ions



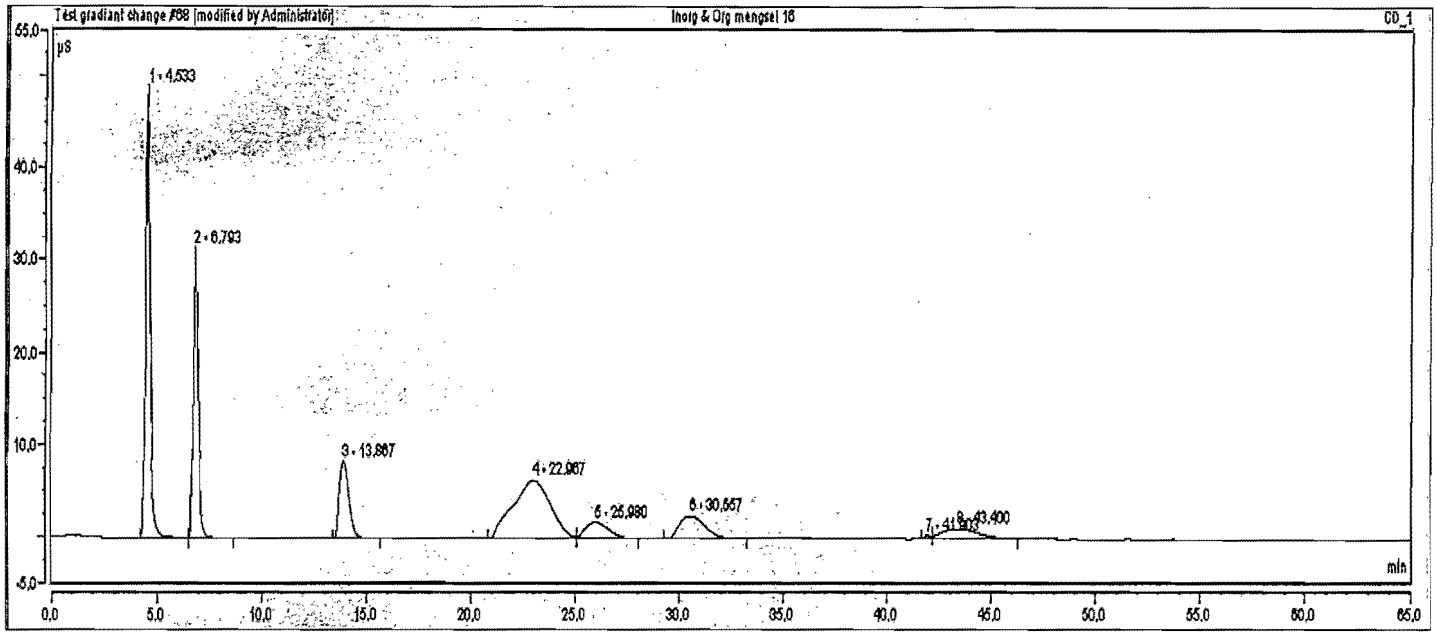
Chromatogram D.14: Gradient program nr. 2



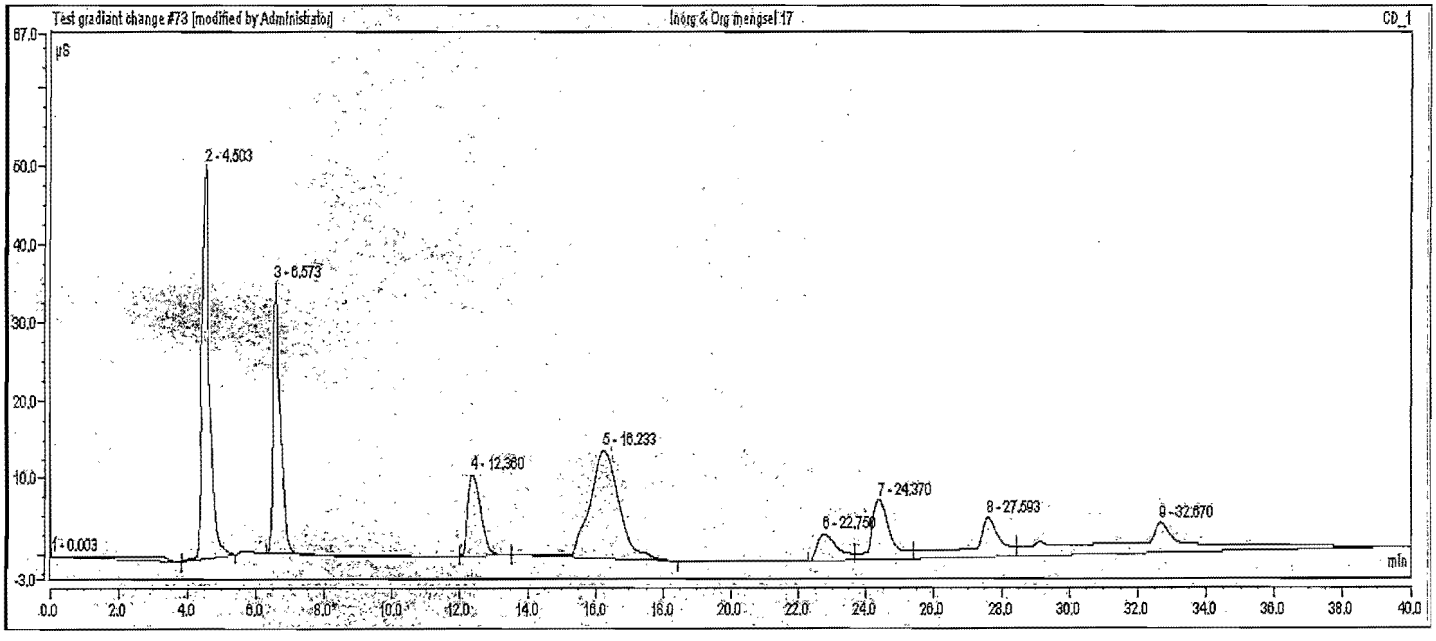
Chromatogram D.15: Gradient program nr. 4



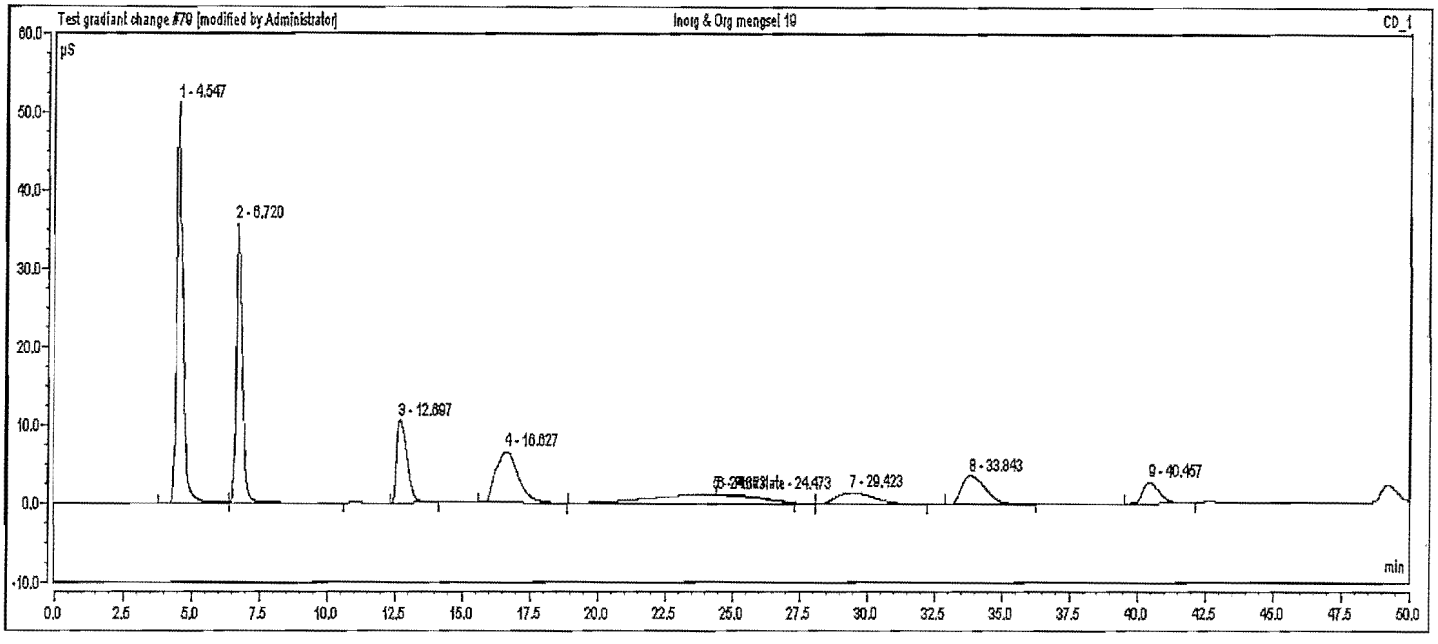
Chromatogram D.16: Gradient program nr. 5



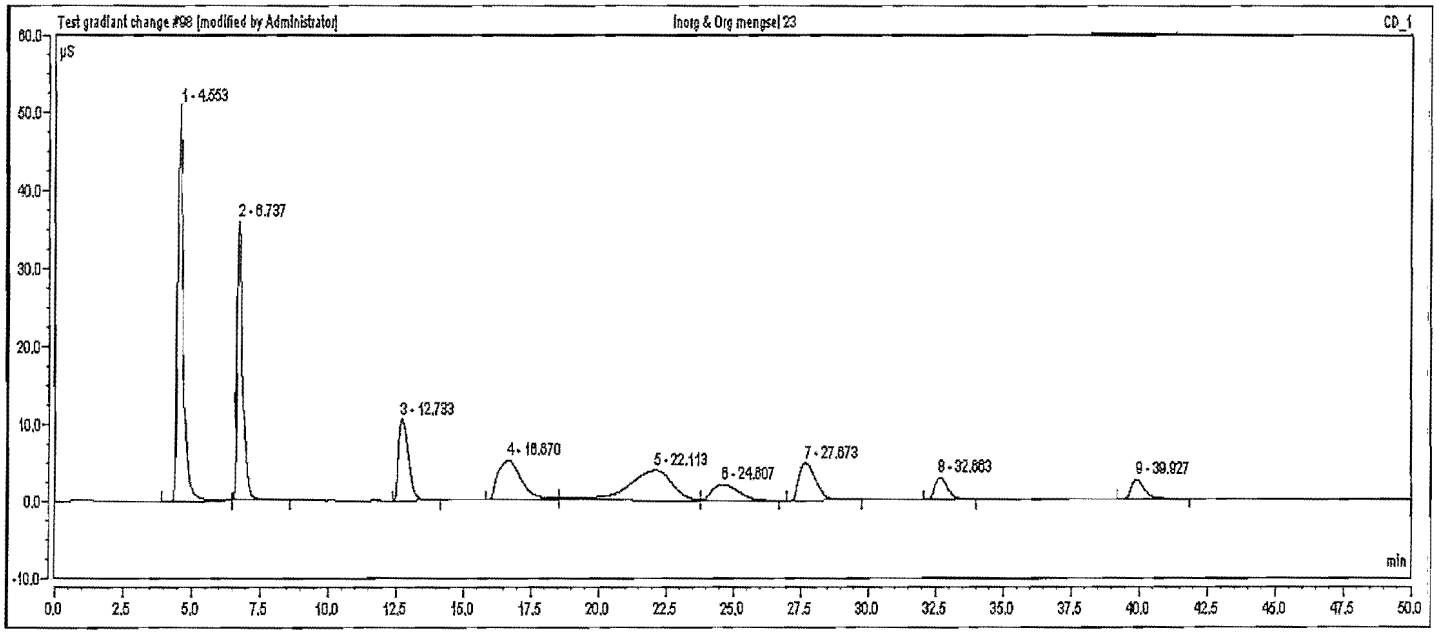
Chromatogram D.17: Gradient program nr. 14



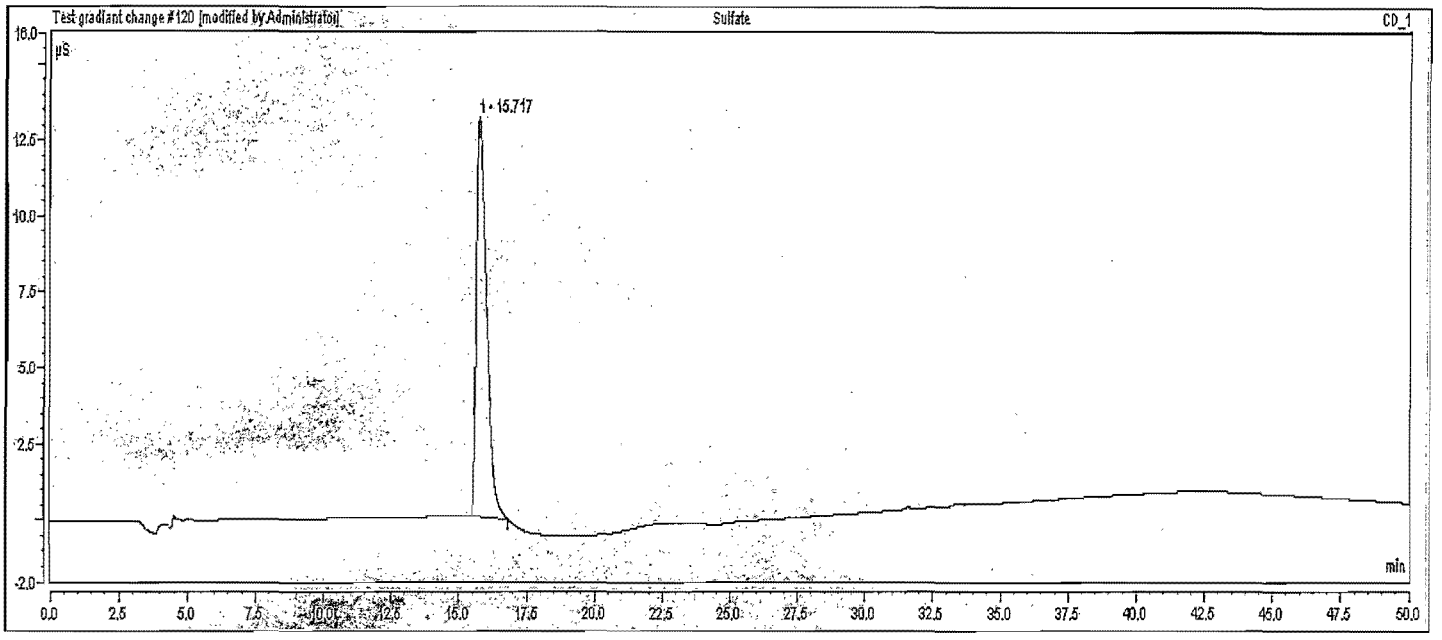
Chromatogram D.18: Gradient program nr. 15



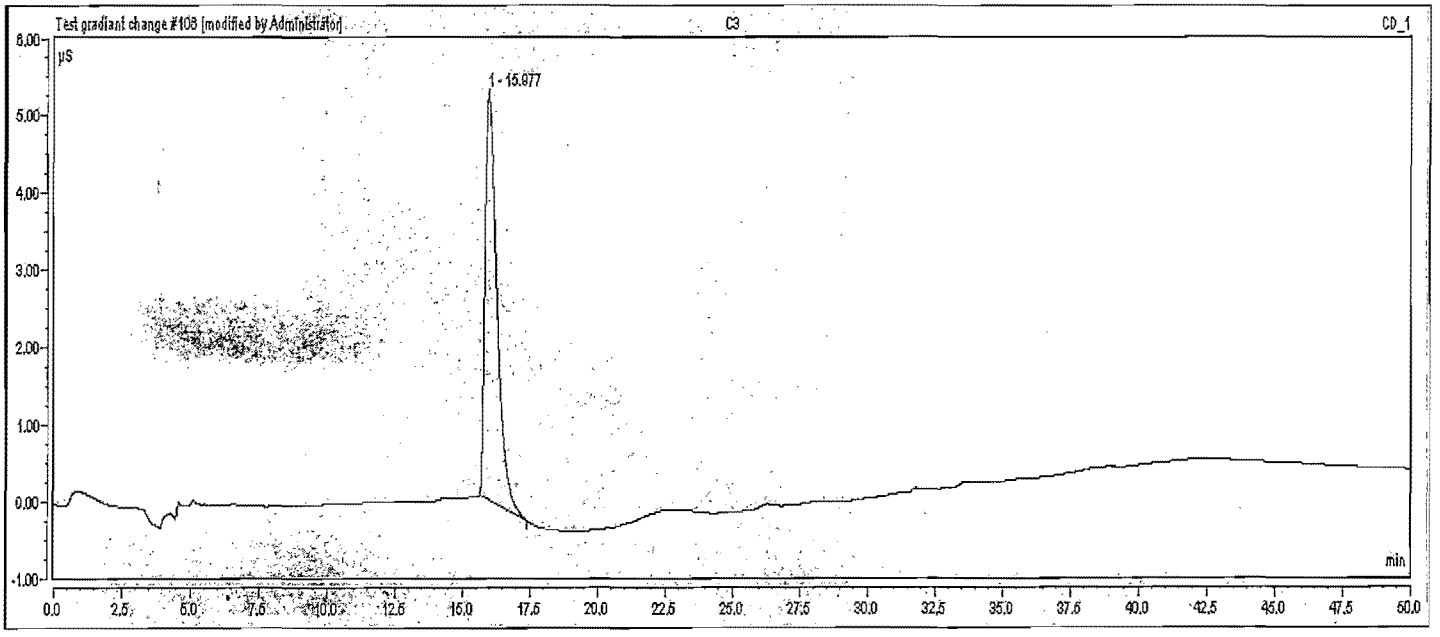
Chromatogram D.19: Gradient program nr. 17



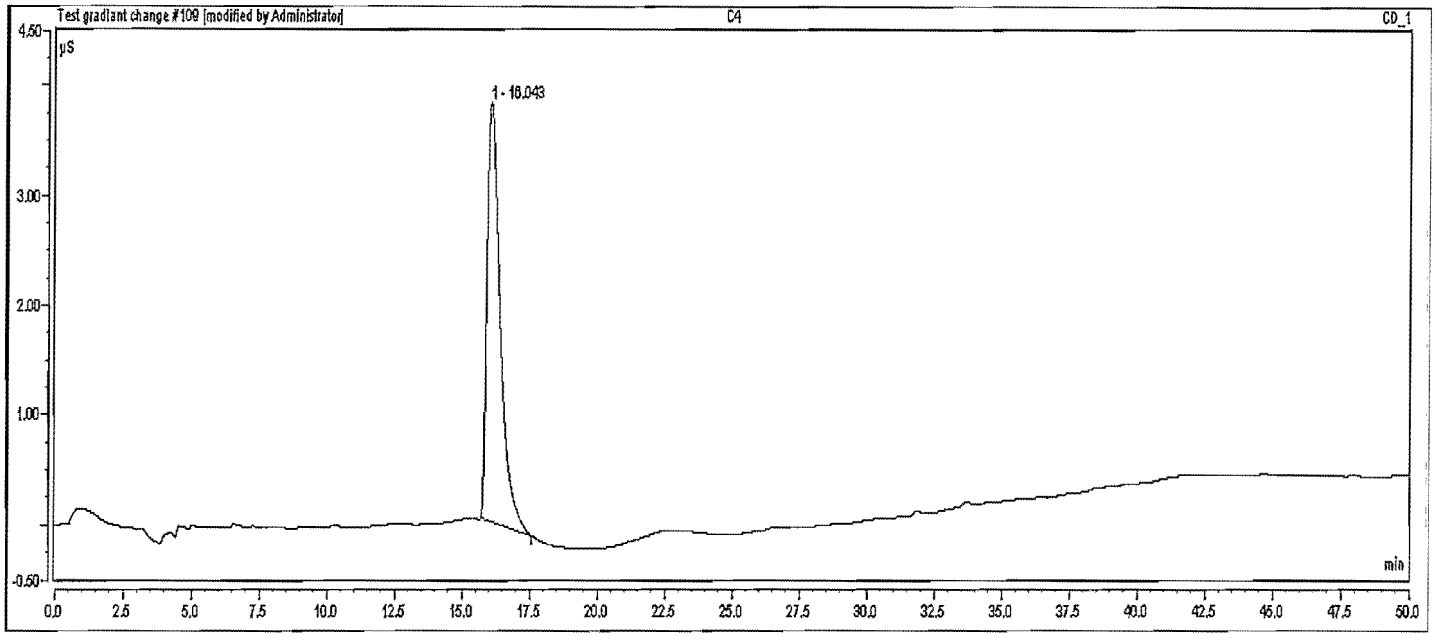
Chromatogram D.20: Gradient program nr. 21



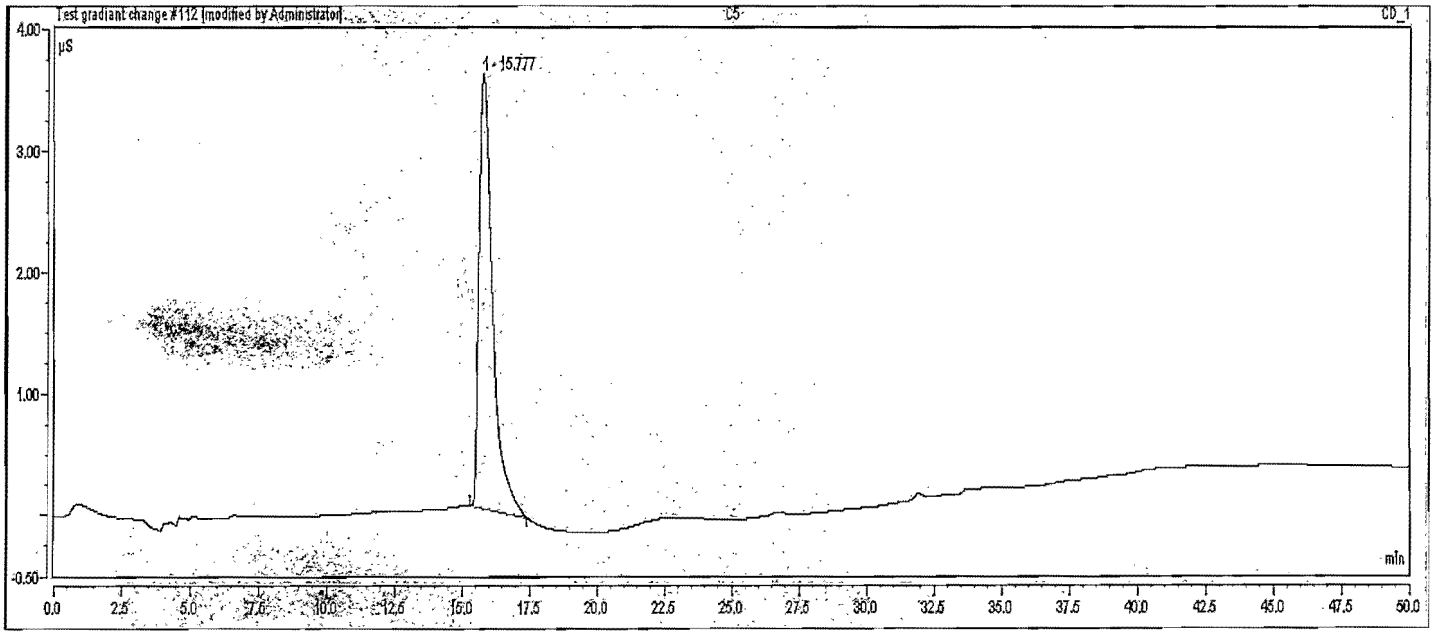
Chromatogram D.21: Sulphate eluted with gradient program nr. 21



Chromatogram D.22: C_3 eluted with gradient program nr. 21



Chromatogram D.23: C_4 eluted with gradient program nr. 21



Chromatogram D.24: C_5 eluted with gradient program nr. 21