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# *Scientia Chromatographica*

2014 | Volume 6 | Número 1

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*on the occasion of his 80th birthday*


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EDITORIAL

# Happy Birthday

**Professor Harold M. McNair**
80 years old

This special issue, as well as the next issue of *Scientia Chromatographica* yields a tribute to Professor Harold McNair, Emeritus Professor at the Virginia Polytechnic Institute and State University, Blacksburg, VA, USA, on the occasion of his 80th birthday. In addition to being an internationally recognized scientist in the separation science arena, Professor McNair is a member of the Editorial Advisory Board of *Scientia Chromatographica* since its conception and first release.

The editors, members of the Editorial Board and readers of *Scientia Chromatographica* are happy to greet him on this occasion and wish him many happy years to come!

**Fernando M. Lanças**
*Editor*

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GUEST EDITORIAL

# Tribute to Harold M. McNair on the Occasion of his 80th Birthday

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My earliest memorable experience with Professor Harold M. McNair was in October, 1983, at the International Symposium on Advances in Chromatography, which was held in Amsterdam, The Netherlands. I was a young faculty member then at Brigham Young University, and just beginning to meet the "icons" of chromatography. When I started as a graduate student at Indiana University working in capillary column gas chromatography, the first book I read was "Basic Gas Chromatography," which was authored by Harold in the 1960s. So, as you can imagine, I was excited to see him in Amsterdam. The social activity at the Symposium, as I remember, was a dinner in a rustic structure that catered toward tourists by having artisans under the same roof working on their specialty crafts. Harold went out of his way to spend some time with me explaining the Dutch customs and even purchased and presented to me a Dutch Delft blue and white vase as a gift, which I still display in a prominent place at home. Early on, I gained a great appreciation for Harold's passion for welcoming and mentoring newcomers to the field of chromatography.

Harold has always first been an educator throughout his career, whether in industry or academics. He is driven to teach the principles behind the techniques much more than just how they work. His talks at scientific meetings are always presented like a teacher in a classroom; his explanations are carefully planned and well-articulated, and he always looks for feedback, understanding and learning. This undoubtedly is the basis of his overwhelming success as a short course instructor as well as a university professor. He never seems too busy to answer questions or give advice, whatever the situation is, and to whoever is looking for help. Whenever you are in the presence of Harold, you always feel welcome and appreciated – this is a great personal gift that he gives to the chromatography community in addition to his scientific expertise and insights. I thank him for his influence on me personally, and grateful that he ranks high as friend and associate in my chromatography world.

**Milton L. Lee**
*Brigham Young University, USA*

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TRIBUTE

# Professor Harold M. McNair: A Life dedicated to separating chemical species and unifying the Human beings.

**Fernando M. Lanças**

University of São Paulo
Institute of Chemistry at São Carlos
13560-970 - São Carlos (SP) Brasil

*Harold Monroe McNair* was born in Miami, Arizona (USA). He studied at the University of Arizona, Tucson, graduating with a BS degree (*Magna cum Laude*) in Chemistry in 1955. Shortly after, in 1957, he received his M.S. degree (with a thesis in electrochemistry), and in 1959 his Ph.D. degree (with a thesis on gas chromatography), both degrees in Analytical Chemistry from Purdue University, West Lafayette, Indiana, USA. Shortly after, he spend one year as a Fulbright Postdoctoral Fellow at the Eindhoven Technical University, Eindhoven, The Netherlands, in the laboratories of Professor A. I. M. Keulemans. In this place he first met Marjike, the laboratory secretary that became his wife for the whole life. Harold uses to tell that Professor Keulemans knew very well how to select the most beautiful secretaries and the cleverest co-workers. Another secretary to work on this same laboratory was Mariet, who married Professor Karel Cramers, the successor of Professor Keulemans as the head of this laboratory. Asked recently in an interview who first influenced him to work with gas chromatography, Harold quickly listed Professor A.I.M. Keulemans, Dr. A.J.P. Martin (Nobel Prize in Chemistry) and Dr. Steve Dal Nogare. In a recent publication, he describes his experiences working together with these icons of chromatography[1].

Returning from Eindhoven, Harold was hired at Esso Research & Engineering, in December 1960. Just one year later, he joined F & M (later Hewlett-Packard Division in Wilmington, USA, now Agilent Technologies) with the responsibility of setting up their European operation. In 1963, Harold moved to Wilkens Instruments (later Varian Aerograph and now fragmented in different companies), as their Director of International Operations in Europe. After already living four year in Europe, in 1966 he was transferred to the company's headquarters in Walnut Creek, California, as their Director of Worldwide Marketing. In 1968, after the death of Steven Dal Nogare, Harold took his most important professional decision and returned to the academia environment by joining Virginia Polytechnique Institute and State University (VPI&SU), in Blacksburg, VA, USA. He became Professor of Chemistry in 1971 and served as the head of the Chemistry Department between 1990 and 1992 were he is now an Emeritus Professor.

Asked about what he would like to emphasize from his quite long research achievements, Harold pointed out[1,2]: the report on the first capillary gas chromatography–mass spectrometry (GC–MS) results in 1961; the introduction of temperature programmed liquid chromatography (LC) in 1981; the use of mobile-phase modifiers to stabilize retention times on silica gel; the development of the first directly coupled LC–GC experiment using two independent computers in 1981; the identification of the role of pH in capillary zone electrophoresis (CZE); and the early work on the analyzes of steroids in urine by gas chromatography time-of-flight mass spectrometry (GC–ToF-MS).

In spite of being the author or coauthor of over 100 scientific and technical papers, 14 book chapters and six books (two in Spanish), probably his most important activities are those of a teacher, both at VPI and outside. At VPI, over 50 students have completed MS and Ph.D. theses under his supervision, being his graduates much sought by research institutions and industrial laboratories. A large number of Pos Docs supervised by him, are now leaders in the separation sciences in several countries around the world, giving continuity to him work initiated at the Virginia Tech almost half century ago. He has being also actively engaged in giving short courses on various aspects of chromatography for the American Chemical Society (ACS) and other organizations. He participated in 1967 in the first ACS Short Course ever offered (on GC); since then, he has taught at more than 180 courses[1-3]. As teaching aids, he prepared several educational movies and audio-visual programs on gas and liquid chromatography. A most representative moment of his professional carrier would have to include his main scientific passion: how to explain to a novice the importance of chromatography, as in the Chromedia video course on Gas Chromatography[3] (Figure 1).


**Figure 1.** Picture from a Chromedia video course on Gas Chromatography[3]. http://www.youtube.com/watch?v=ljz43nJNLFs

A summary of Dr. McNair's awards during his professional carrier would include the IR-100 Award as the co- inventor of the CIRA GC/IR system (1975); the VPI Alumni Teaching Award (1983); the Eastern Analytical Symposium's Award in Chromatography (1989); the K.P. Dimick Award (1991); the Tswett Medal (1993); the Dal Nogare Award (2001); the Horvath Medal (2003) and the LCGC Lifetime Achievement Award (2009); amongst others. In 1986 he received the first COLACRO Medal for Contributions to Chromatography in Latin America (Figure 2).

In addition to his other scientific activities, Dr. McNair contributed on the Editorial Boards of Analytical Chemistry, Chromatographia, Journal of Chromatography, Journal of Chromatographic Science, Journal of High-Resolution Chromatography, Journal of Liquid Chromatography, Journal of Pharmaceutical and Biomedical Analysis, and Scientia Chromatographica. He is actively involved in the organization of a number of international meetings and symposia, being one of the initiators of the biannual COLACRO (**Co**ngresso **L**atino-**A**mericano de **Cro**matografia) Symposia (Figure 3).

**Figure 2.** Professor Harold McNair (left) receiving from Professor Fernando Lanças (right), Chairman of the Latin American Symposium on Chromatography, the first COLACRO Medal. Rio de Janeiro, 1986.

I met Professor McNair for the first time in April 1981, when he was at the University of Campinas (UNICAMP), Brazil, as a consultant for UNESCO. I was defending my Ph.D. Thesis and Harold got a sit at the public to hear my presentation. After the defense we had a very nice and extensive talk – obviously about chromatography and teaching. He really incentivize me to visit him at the Virginia Tech to develop a research project in chromatography and get involved in his


**Figure 3.** Third Latin American Symposium on Chromatography held in Brazil, 1990, showing the Permanent Organizing Committee; from left to right: Harold McNair; Pat Sandra; Fernando Lanças (Chairperson) and Karel Cramers.

courses. He was so enthusiastic and convincing that at the end of the same year, I started a 2 years visit program as a Visiting Professor with Professor McNair in Blacksburg, VA, USA.. Upon finishing my visit I returned to Brazil and shortly after (less than 2 years later) we started together – with the help of two other Icons of chromatography Professor Karel Cramers and Professor Pat Sandra - the now successful COLACRO (Latin American Congress on Chromatography) meeting, the most important forum for the discussion of Separation Sciences in Latin America. During the period after my first visit to his laboratory, he had the opportunity to visit me several times at the University of São Paulo, Brazil, always incentivizing my progress in the Academic area. Several of my former graduate students had the opportunity to visit his laboratory at VPI, either for a short time or as one year Pos Doc. All of them had an excellent professional opportunity and always acknowledges Professor McNair not only for the excellent scientific work they developed in his laboratory but also for his kindness in welcoming international visitors and students.

While working in his laboratory back in 1982 and most 1983 I had an excellent opportunity to interact with his students as well from other laboratories, frequently coming to consult him about chromatography. The interaction created by him within his students presented the ideal atmosphere for the development of outstanding research programs in chemistry, together with training on how to become a **T**eacher (with capital T). Also the human being side was never neglected and he always tried to advise the students on how to became a scientist in the complete concept of the term, thus including also our role in the Society, particularly our responsibilities.

In addition to my personal experience in interacting several times with Professor McNair, I had the great opportunity to participate in several events together with him, particularly in Latin America including Brazil (several times), Argentina (several times), Chile (couple of times), Colombia, Venezuela, Mexico, and so on. Based on that I can ensure that he is the most knowledge American scientist in Latin America. Through my participation in many international meetings in USA (in special PittCon and the International Symposium on Chromatography) and Europe, I could also be a testimony about how many people know and interact with him, including scientists from Russia, Japan, China, India, and so on.

In short, it has been a great feature in my professional career and personal life to have the opportunity to interact with Professor McNair during several decades.

On the occasion of his eighty birthday, the Editor and the co-Editors, publisher and readers of *Scientia Chromatographia* – representing the Latin American researchers working on Separation Science – joins our colleagues from all over the world to wish Professor McNair many more years of productive work.

To wrap up this tribute to Professor Harold McNair in acknowledgement to his immensurable contribution to the *separation of molecules and unification of human beings*, I would like to add my personal greetings to him as a friend who had the privilege to participate in many wonderful moments of his life, enjoying his advisement, cooperation and friendship.

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# Trace Analysis in the Field Using Gas Chromatography-Mass Spectrometry

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**Abstract**

Trace analysis of samples in the field, including air, headspace, and water (i.e., drinking and waste), as well as solid matrices and surfaces, for volatile organic compounds (VOCs) and semi-VOCs is a growing demand. Detection of target analytes, such as pesticides, polycyclic aromatic hydrocarbons (PAHs) and the natural compounds geosmin and 2-methyl isoborneol at ppb and ppt levels can be accomplished using simple sample preparation methods and gas chromatography-mass spectrometry (GC-MS). Solid phase micro extraction (SPME), solid phase extraction (SPE), thermal desorption, needle trap and purge-and-trap have become indispensable methods for field sampling when GC-MS is used for separation and detection. Sensitivity, selectivity, speed of analysis and simplicity of advanced in-field sample preparation devices have improved on-site trace analysis. Example analyses reported in this work involving approximately 54 VOCs were shorter than 20 min for drinking water, waste water and solid waste samples at the ppt to ppb concentration levels. Geosmin and 2-methyl isoborneol were detected at less than 10 ppt in water samples within 20 min. Pesticides including lindan, endrin, heptachlor, heptachlor epoxide, methoxychlor, malathion, carbaryl, benfluralin and chlorthal dimethyl, as well as PAHs such as naphthalene, fluorene, phenanthrene, acenaphthalene, acenaphthylene, anthracene, pyrene and chrysene were sampled and detected at concentrations in the low ppb in water samples within 15-20 min. Other organo-chlorine and organo-phosphorus pesticides in fresh tea-like leaves were also detected at ppb levels. VOCs can be detected at low ppb concentrations using a needle trap, and even lower with a higher flow thermal desorption tube. Dimethyl sulfide in water was determined at low ppb concentration. These analytical methods are generally applicable to other target analytes in environmental samples.

**Keywords:** Field detection; Trace analysis; Sample preparation; GC-MS; SPME; SPE; Needle trap; Purge-and-trap; Thermal desorption

## 1. Introduction

Development of field-portable gas chromatography-mass spectrometry (GC-MS) instrumentation requires simple, robust hardware and complementary methods for sample preparation and introduction[1,2]. Often, analysts in the field do not have in-depth training in pre-chromatographic chemical sample preparation such as extraction, clean up, concentration and derivatization. Furthermore, they may be required to wear protective equipment that limits dexterity and control over fine objects. To complicate matters, the deployed sampling device(s) must accommodate gas, liquid or solid samples. Obviously, several, simple sampling devices for GC-MS analysis in the field are preferable to multiple, complex sampling devices. In-field analyses that can provide testing results within minutes or even seconds have always been in demand in analytical chemistry. This is especially the case for powerful techniques such as GC, GC-MS, Fourier transformed infrared (FTIR) spectroscopy and Raman spectroscopy. It is easy to recognize the importance of rapid detection of chemical warfare agents[3] deliberately released by terrorists, or chemical contamination of food and/or water in manufacturing, storage or distribution facilities.

Sample preparation methods for field analysis must be simple and straightforward due to limited availability of analytical tools, chemicals and well-controlled laboratory conditions. In addition, sample treatment times should be as short as possible, and the amounts of chemicals, especially those that are hazardous, sensitive or toxic, should be minimized. Among such sample preparation methods is solid phase micro-extraction (SPME), which is considered by many analysts to be the simplest sampling tool for a wide variety of samples; SPME has been used in both static or dynamic sampling modes for gas, liquid and solid samples. For the latter, the solid sample must be dissolved or suspended in a liquid, or its headspace must be sampled. SPME is based on partitioning of analytes between the sample matrix and a sorbent phase, which is typically a coating on a fused silica or flexible metal (i.e., nitinol) fiber. After sampling, the SPME fiber is retracted inside a needle for sample introduction into the GC-MS, and then re-extended inside the heated injection port for desorption. Using SPME, additional sample preparation steps and extraction solvents are avoided[4-6], thus simplifying sample preparation and minimizing sample handling. Different fiber coatings are designed to provide selectivity and concentration of target analytes.

Headspace SPME has been widely used for VOC sampling from aqueous and solid matrices[7-10], mainly because (a) the headspace medium (i.e., air or inert gas) is compatible with GC-MS, (b) headspace SPME is easy to perform in field operations[11] and (c) the GC-MS system is protected against contamination from dirty matrices and subsequent extensive cleanup[12]. Headspace SPME is generally performed in the static or equilibrium mode. The disadvantage of equilibrium sampling is the inherent limitation in sample size and, hence, detection limits.

Solid phase extraction (SPE) tubes containing a variety of sorbents have typically been used for the analysis of water samples. Such traps have typical dimensions of 6 cm x 4.6 mm i.d., and are packed with from 0.3-1.2 g of sorbent that allow the analysis of approximately 1 L volumes of water with a flow rate from 20-30 mL/min. Tubes containing poly(dimethylsiloxane) (PDMS) particles are simple to fabricate and use for detecting semi-volatile compounds such as pesticides, polycyclic aromatic hydrocarbons (PAHs), geosmin, etc., in water samples.

SPE, when used for air sampling, is generally referred to as thermal desorption, and materials such as Tenax TA, various Carboxens and/or Carbopacks and activated charcoal are used as sorbents. Elevated temperatures are used to desorb analytes from the sorbent into the injection port of the GC-MS system. Thermal desorption tubes are used in numerous air monitoring applications in a wide variety of industries including industrial hygiene, environmental air monitoring, odor profiling in the food and flavor industry, defense and forensic applications, and material emissions testing.

They can also be used in the analysis of a variety of matrices other than air, for example, the headspace above solids (powders, fibers, films and granules), resins, pastes, liquids and emulsions. Sampling of VOCs using thermal desorption tubes can be achieved using either active (pumped) or passive (diffusive) conditions. The selectivity is dependent on the choice of sorbent material, the sampler design and the operating conditions for the specific analytical task[17].

The needle trap is a recent development that has advantages adopted from both thermal desorption tubes and SPME, in that a needle, which is small enough to be directly inserted into the injection port of a GC-MS system for desorption is packed with a sorbent material. The design of the needle trap provides higher sample capacity than SPME and the sorbent material is better protected from damage since it remains inside the needle. The small needle trap also helps to minimize GC injector contamination. A typical example of a needle trap is an 8.89 cm long 22-guage stainless steel needle packed with divinylbenzene (DVB) particles. A small hole drilled in the side of the needle approximately 30 mm from the needle end (i.e., side-hole needle trap) allows carrier gas to pass through the needle and into the injector during the desorption step[13]. If there is no side hole in the needle, the purge gas for desorption must be introduced directly into the needle through a fitting or valve to carry the analytes out of the needle and into the injection port.

Different types of packing materials have been used in needle traps, including quartz wool for sampling particulate matter and aerosol; single layers of Tenax TA, Carboxen, PDMS and DVB; or combined layers of these sorbents. Tenax TA and various Carboxens are typically used for sampling VOCs[14]. Needle traps can also be used in combination with higher capacity thermal desorption traps for semi-volatile analyte analysis. The sampling volume and flow rate are important parameters to consider for improving overall sampling efficiency and reproducibility of needle traps[14-16].

Purge-and-trap systems are the most frequently used preconcentration devices for analysis of VOCs in water samples[18-20]. They are typically used as automated headspace thermal desorption systems. Purge-and-trap systems provide advantages of high sensitivity, precision and automation; their main disadvantage is complexity compared to most other techniques mentioned above. However, purge-and-trap combined with thermal desorption can be simplified for use in the field.

In this paper, we describe the development of equipment and methods to facilitate use of the various sampling techniques described above in solving challenging field applications of interest. With proper implementation, these techniques can be effectively used in the field to determine trace levels of volatile and semi-volatile target analytes in complex matrices.

## 2. Experimental

### 2.1. Chemicals

Standard reference compounds used in this study, including pesticides, PAHs, VOCs, dimethyl sulfide and geosmin were obtained from Sigma-Aldrich (St. Louis, MO, USA). The sorbent materials, Tenax TA and Carboxen were obtained from Sigma Aldrich. The PDMS elastomer and its associated curing agent were from Dow Corning (Midland, MI, USA). PDMS particles were prepared by curing, heating, grinding and sieving as described previously[21].

### 2.2. Equipment

DVB/PDMS SPME fibers from Supelco (Bellefonte, PA, USA) were used in a CUSTODION SPME fiber holder (Torion Technologies, American Fork, UT, USA). Two types of needle traps, with and without side hole, were packed with different sorbent materials, including Tenax TA, different types of Carboxen, and PDMS, depending on the specific target analytes and sample matrices. The needle traps

were fabricated and packed at Torion. Figure 1 shows diagrams of both needle trap types. Sampling using the needle trap was performed by flowing an air or vapor sample through the sorbent bed at ambient or other specified temperature at a suitable flow rate, which was controlled using a simple, adjustable vacuum or pressure source. After sampling, target analytes were introduced directly into the GC-MS by inserting the needle trap into the injection port in the same manner as inserting a syringe needle.

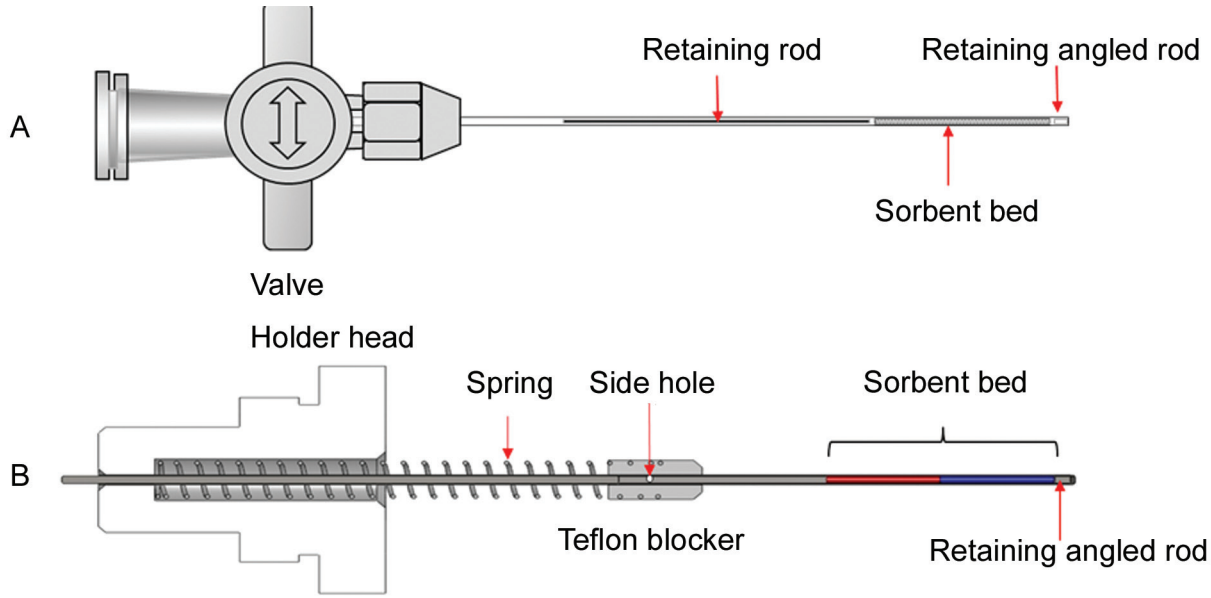


**Figure 1.** Diagrams of needle traps (A) without and (B) with side hole. Needle o.d. = 1.07 mm, needle i.d. = 0.85 mm, total needle length = 82 mm, rounded needle opening = 0.15 mm, retaining angled rod o.d. = 0.72 mm.

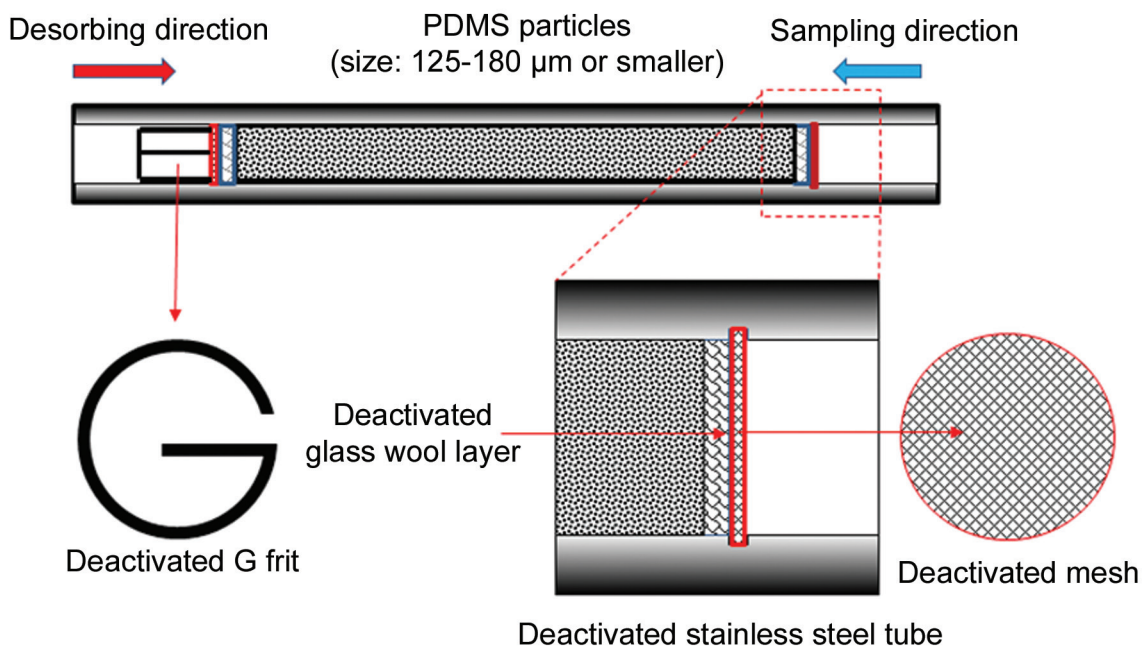


**Figure 2.** Diagram (not to scale) of a stainless steel SPE/thermal desorption sampling tube.

Conventional SPE/thermal desorption tubes (8.89 cm x 0.635 cm i.d. glass or stainless steel) were prepared at Torion (Figure 2). In this work, the tubes were packed with PDMS particles; however, other sorbents can also be used. When the SPE/thermal desorption tubes were used in this study to improve the detection limits for trace analytes, the compounds trapped in the tubes had to be transferred to the needle trap in order to introduce them into the GC-MS system (Figure 3).

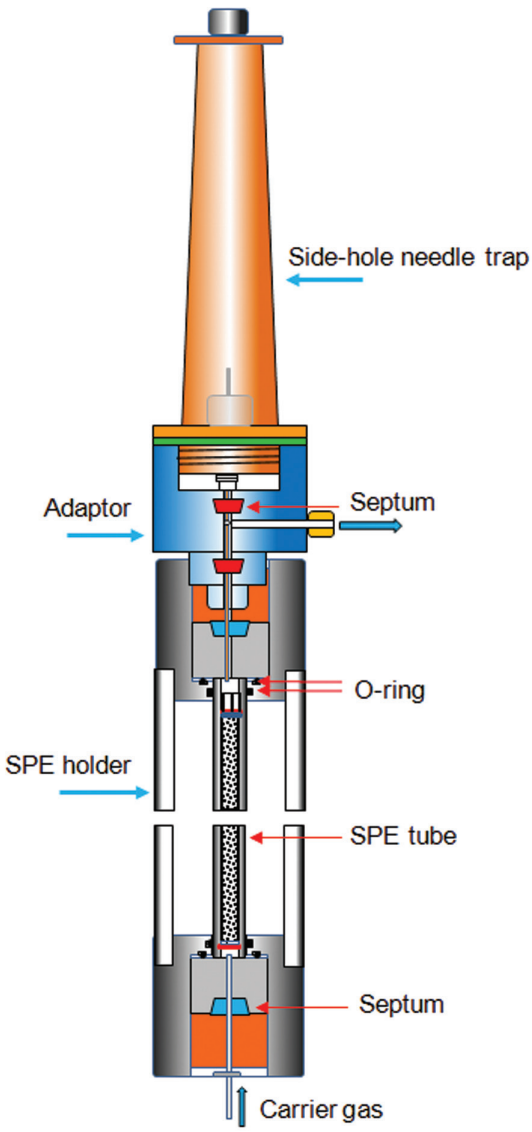


**Figure 3.** Diagram of device for connecting an SPE/thermal desorption tube to a needle trap for sample transfer before injection into the GC-MS.

Sample transfer to the needle trap occurred by thermal desorption using a portable desorber unit (FUZION, Torion Technologies).

SPE tubes for sampling water were packed with cross-linked PDMS particles. Using this packing material, solvents used for washing and eluting analytes were typically methanol or mixtures of methanol and water, or acetone and water. PDMS particles were prepared in the size range from 125-150 or 150-180 µm for extracting pesticides, PAHs and geosmin in water. The sampling and eluting flow rates were controlled using a commercial SPE syringe and adapter for 1, 3 and 6 mL SPE tubes, Supelco) or a small diaphragm vacuum pump (PU 1781, KNF Neuberger, Trenton, NJ, USA)

Four simple purge-and-trap systems were designed for use in the field using either SPE/thermal desorption tubes or needle traps. Figure 4 shows schematic drawings of the purge-and-trap systems, which were used with a gas supply (Figure 4A), vacuum pump (Figure 4B) and gas-tight syringe (Figures 4C and 4D). The sampling flow rate and volume are controlled by the operator. The system can be easily constructed using standard laboratory parts; significantly different volumes can be sampled simply by changing the size of the sample/purge vessel.

GC-MS analyses in this study were conducted using the TRIDION-9 (Torion) which contains a low thermal mass, resistively-heated GC column and a toroidal ion trap mass spectrometer that covers a mass range from 43 to 500 Daltons. All samples were injected using either an SPME fiber or a needle trap. The GC column was a 5 m x 0.1 mm i.d. metal column containing a 0.4 µm film of poly(5% phenyl methylsiloxane) (MTX-5, Restek, Bellefonte, PA, USA). The injector was maintained at either 270 ºC or 290 ºC, and was operated at constant inlet pressure using the split or splitless mode. The column temperature program was 50-290 ºC at either 2 or 1 ºC/s, depending on the sample. The transfer line to the MS was maintained at 250 ºC for all experiments. CHROMION software (Torion)

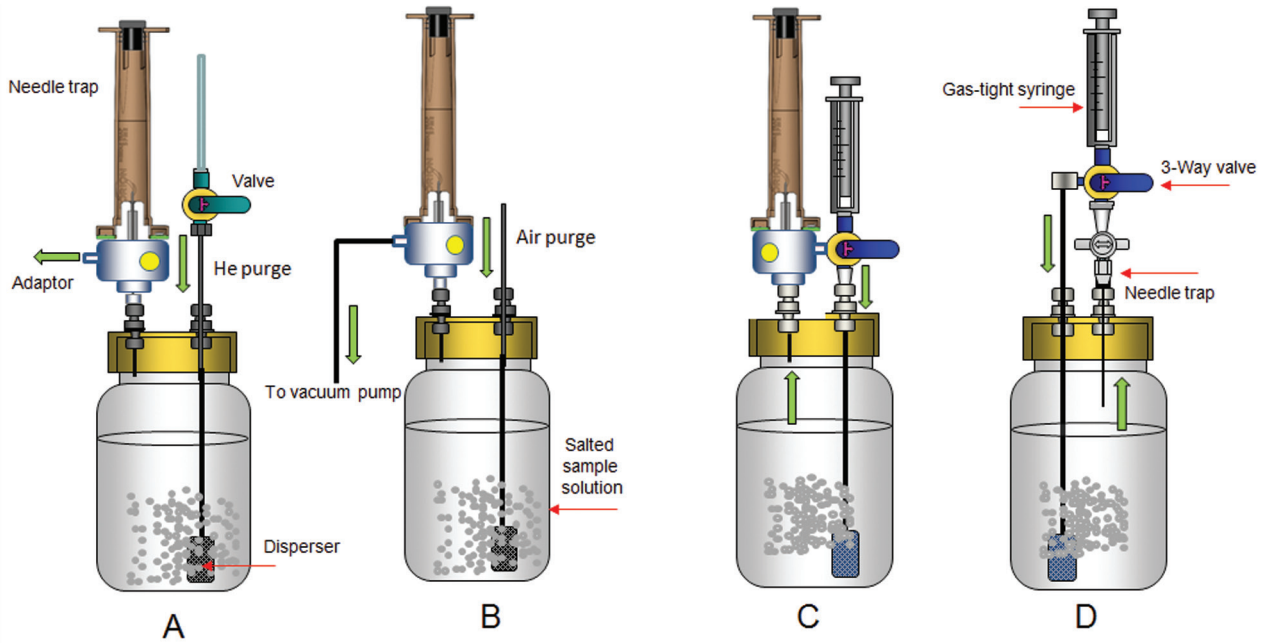


**Figure 4.** Diagrams of purge-and-trap systems used for sampling water with (A and B) gas purge and/or vacuum pump and (C and D) gas-tight syringe.

equipped with deconvolution and quantitation features was used to generate calibration data, and to identify and quantify target analytes down to ppt levels, even in the presence of other compounds at higher concentrations.

## 3. Results and Discussion

### 3.1. Determination of VOCs in water using an external standard mixture

VOCs contribute to major environmental problems such as global warming, stratospheric ozone depletion, photochemical ozone formation and odor nuisance[22]. Trace VOCs in water were detected using a purge-and-trap method that allows for determination of multiple components within a single run in, including sample preparation, analysis and reporting after 20 min. For constructing calibration curves, a 54 component Mega Mix 502.2 (Restek) was spiked into 500 mL of tap water at concentrations ranging from 50 ppt to 1.0 ppb. The purge-and-trap device shown in Figure 4D was used for this work.

Figure 5 shows a total-ion-current chromatogram of the VOCs extracted from 500 mL of water spiked at 200 ppt. The sample was purged through a Tenax TA/CAR 1000 (1.5 mg/1.5 mg 60-80 mesh) needle trap for a total time of 6 min (8 syringe cycles) at ambient temperature (22 °C) and 40 mL/min using a 20 mL gas-tight syringe. Calibration curves of the VOCs showed excellent linearity ($R^2 \geq 0.996$ for the range 50-1000 ppb), which indicates the stability of this purge-and-trap approach, although there was undoubtedly some variation in time and volume for each cycle.

### 3.2. Trace detection of geosmin in water

Geosmin is a naturally occurring compound that is released when soil-present microbes die. Geosmin is a contributor to the strong scent that occurs when rain falls after a dry weather spell. Communities whose water supplies depend on surface water can periodically experience episodes of unpleasant tasting water when a sharp drop in the population of these bacteria releases geosmin into the water. These compounds are responsible for the earthy, musty odor.

For initial examination of the feasibility of detection of geosmin in water, tap water spiked with 20 ppt geosmin was drawn through a deactivated stainless steel SPE tube packed with PDMS particles (125-180 µm) at ambient temperature and at 25-35 mL/min flow rate

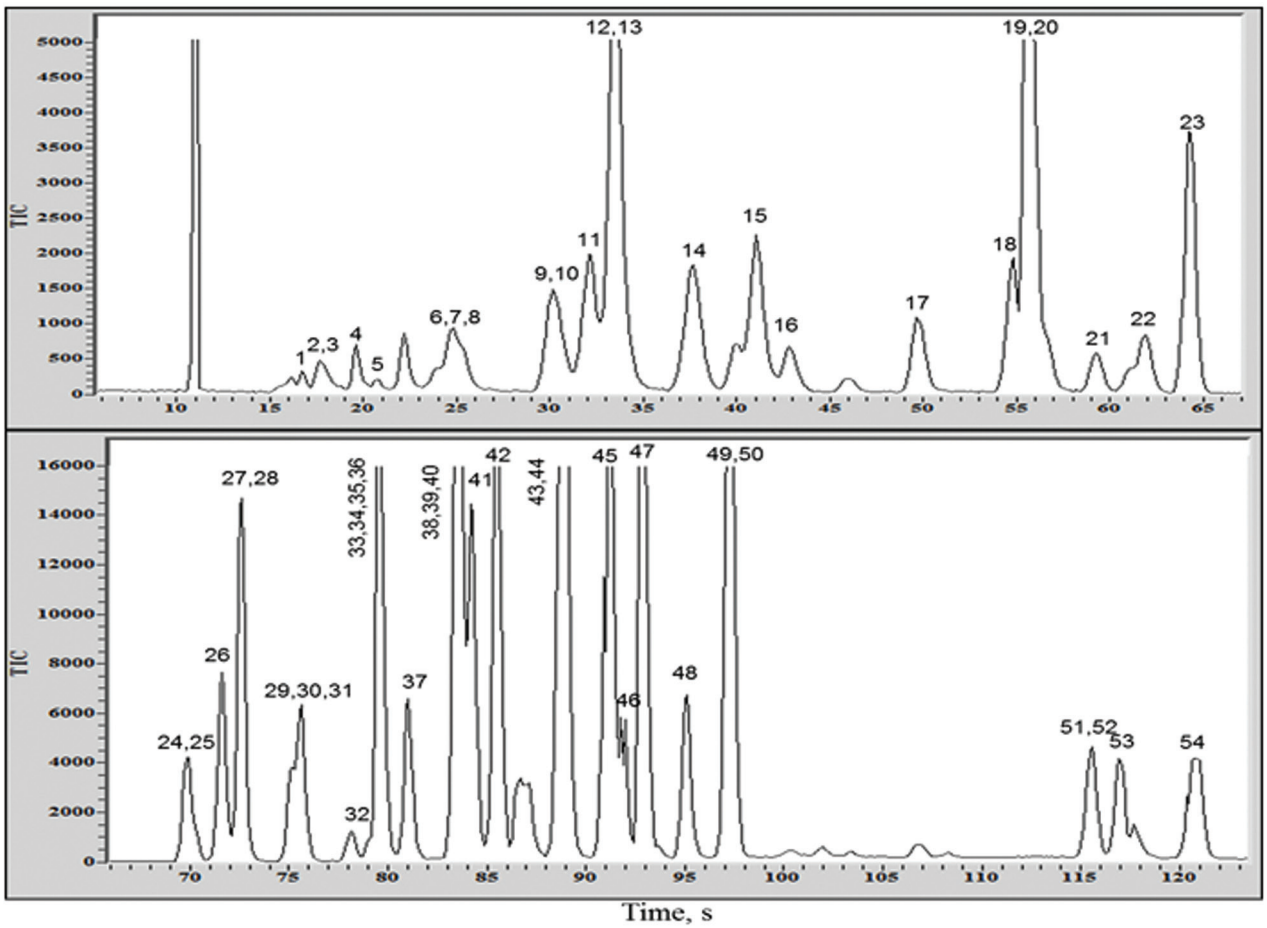


**Figure 5.** Total-ion chromatogram of 54 VOCs in water (200 ppt) using purge-and-trap with a two-segment needle trap. Needle trap conditions: Tenax TA/CAR 1000 (1.5 mg/1.5 mg, 60-80 mesh). GC conditions: 50 °C (10 s), 2 °C/s to 270 °C, 270 °C injector, 18 psi He pressure, 10:1 split mode. See Table 1 for peak identifications.

using a small portable vacuum pump. The target analyte was then transferred into a needle trap packed with the same PDMS using the FUZION desorber unit (Figure 6). Desorption was performed at 200 °C for 10 min at 6 mL/min He carrier gas. Sample introduction into the GC-MS system using the needle trap was conducted at 270 °C for 60 s. Needle traps packed with Tenax TA/CAR 1016/CAR 1003 (1.1/1.6/1.3 mg 60-80 mesh) or PDMS (2.5 mg 125-180 µm particles) were evaluated for comparison; however, the needle containing PDMS gave the best results in terms of peak intensity.

The original stock geosmin solution was diluted using distilled water to prepare solutions that contained 1, 10, 20 and 70 ppt (ng/L) geosmin. These solutions were used to develop calibration curves. Three replicates at each concentration were analyzed and included in the calibration data. Good linearity and sensitivity were obtained as shown in Figure 7. After the method was optimized, water samples were collected from a local, large fresh-water lake, from a small creek that flows into the lake, and a larger river that also flows into the lake. Aliquots of each of the samples were analyzed as received. No geosmin was detected in the creek water or river water samples; however, geosmin was detected at 2.5 ppt in the lake water sample. This is understandable since the sample was collected in July when the ambient temperature was high. Standard addition analysis was performed for each sample by adding 10 ppt geosmin. Based on the calibration curves, the recovery at the 10 ppt level was 90% or greater.

**Table 1.** Names of VOCs analyzed in Figure 5.

| No. | Component name | No. | Component name |
|---|---|---|---|
| 1 | 1,1-Dichloroethene | 29 | *p*-Xylene |
| 2 | Methylene chloride | 29 | Bromoform |
| 3 | Bromochloromethane | 30 | Styrene |
| 4 | *trans*-1,2-Dichloroethene | 31 | *o*-Xylene |
| 5 | 1,1-Dichloroethane | 32 | 1,1,2,2-Tetrachloroethane |
| 6 | *cis*-1,2-Dichloroethane | 33 | 1,3-Dichloropropane |
| 7 | 2,2-Dichloropropane | 34 | 1,2,3-Trichloropropane |
| 8 | Chloroform | 35 | Isopropylbenzene |
| 9 | 1,2-Dichloroethane | 36 | 1,2-Dibromoethane |
| 10 | 1,1,1-Trichloroethane | 37 | Bromobenzene |
| 11 | 1,1-Dichloropropene | 38 | 2-Chlorotoluene |
| 12 | Benzene | 39 | N-Propylbenzene |
| 13 | Carbontetrachloride | 40 | 4-Chlorotoluene |
| 14 | 1,2-Dichloropropane | 41 | 1,3,5-Trimethylbenzene |
| 15 | Trichloroethene | 42 | *tert*-Butylbenzene |
| 16 | Bromodichloromethane | 43 | 1,2,4-Trimethylbenzene |
| 17 | *cis*-1,3-Dichloropropene | 44 | 1,3-Dichlorobenzene |
| 18 | 1,1,2-Trichloroethane | 45 | 1,4-Dichlorobenzene |
| 19 | Dibromomethane | 46 | *p*-Isopropyltoluene |
| 20 | Toluene | 47 | 1,2-Dichlorobenzene |
| 21 | *trans*-1,3-dichloropropene | 48 | *n*-Butylbenzene |
| 22 | Dibromochloromethane | 49 | *sec*-Butylbenzene |
| 23 | Tetrachloroethene | 50 | 1,2-Dibromo-3-chloropropane |
| 24 | Chlorobenzene | 51 | 1,2,3-Trichlorobenzene |
| 25 | 1,1,1,2-Tetrachloroethane | 52 | 1,2,4-Trichlorobenzene |
| 26 | Ethylbenzene | 53 | Naphthalene |
| 27 | *m*-Xylene | 54 | Hexachlorobutadiene |

### 3.3. Screening for pesticides and PAH compounds

A mixture of pesticides (7 components) and PAHs (11 components) in tap water were detected at the 100 ppt level using a conventional SPE tube containing PDMS particles to isolate the analytes from a large volume (500 mL) at a flow rate of approximately 25 mL/min, similar to what was just described for geosmin detection. A small amount of water remaining after the sample was drawn through the tube was eliminated by keeping the tube under vacuum for 3 min. The analytes were then transferred to a needle trap packed with PDMS using a GC oven with a temperature ramp from 30° C to 275 °C at 25 °C/min, although the FUZION desorber could also have been used. Figure 8 shows the resultant total-ion chromatogram. The detection limits using this method were lower than 100 ppt.

### 3.4. Detection of dimethyl sulfide in water

Detection limit studies were conducted for dimethyl sulfide in water and air using GC-MS. A tri-bed (i.e., Tenax TA/Carboxen 1016/Carboxen 1000) needle trap was used to extract/trap the target analytes and inject them into the GC-MS system. A purge-and-trap procedure was used for water sampling, while air was sampled directly using a needle trap with battery-operated vacuum pump. A standard stock solution of dimethyl sulfide in methanol was prepared at

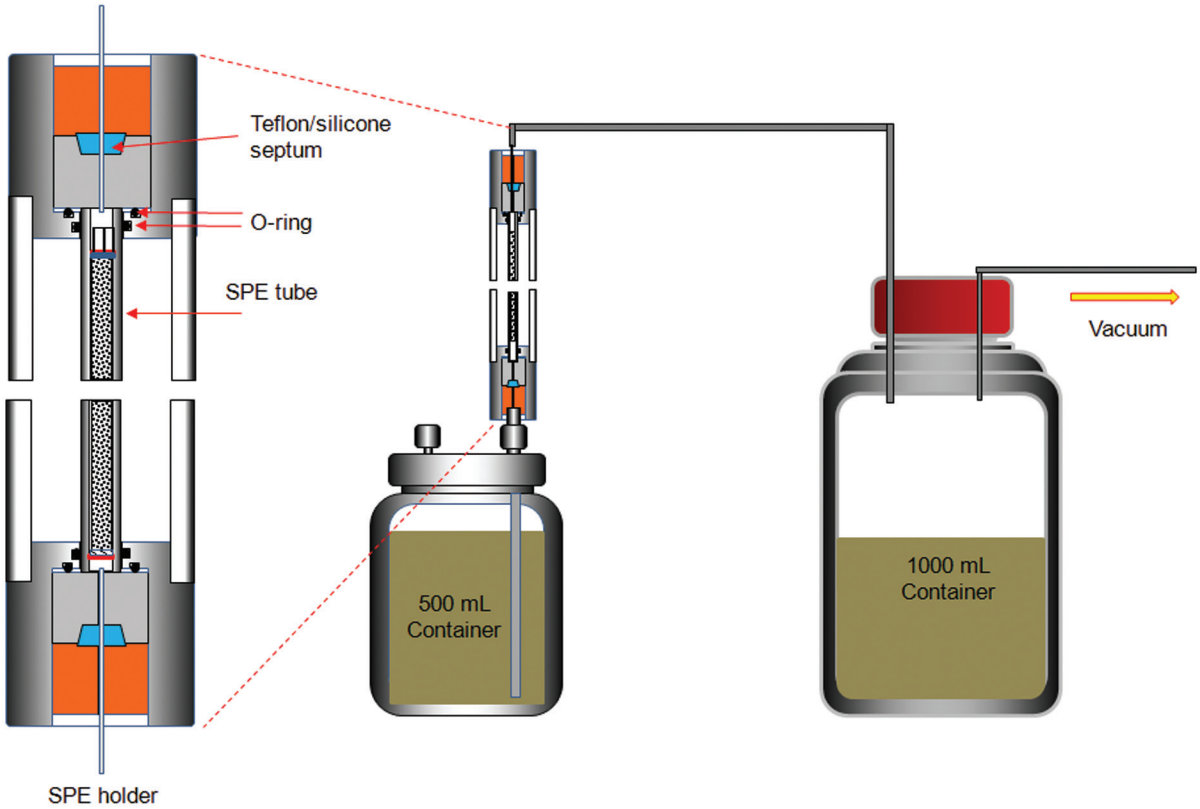


**Figure 6.** Diagram of the set-up for SPE of geomin in drinking water. SPE conditions: 500 mL sample, 25-30 mL/min sampling flow rate at ambient temperature (22°C).

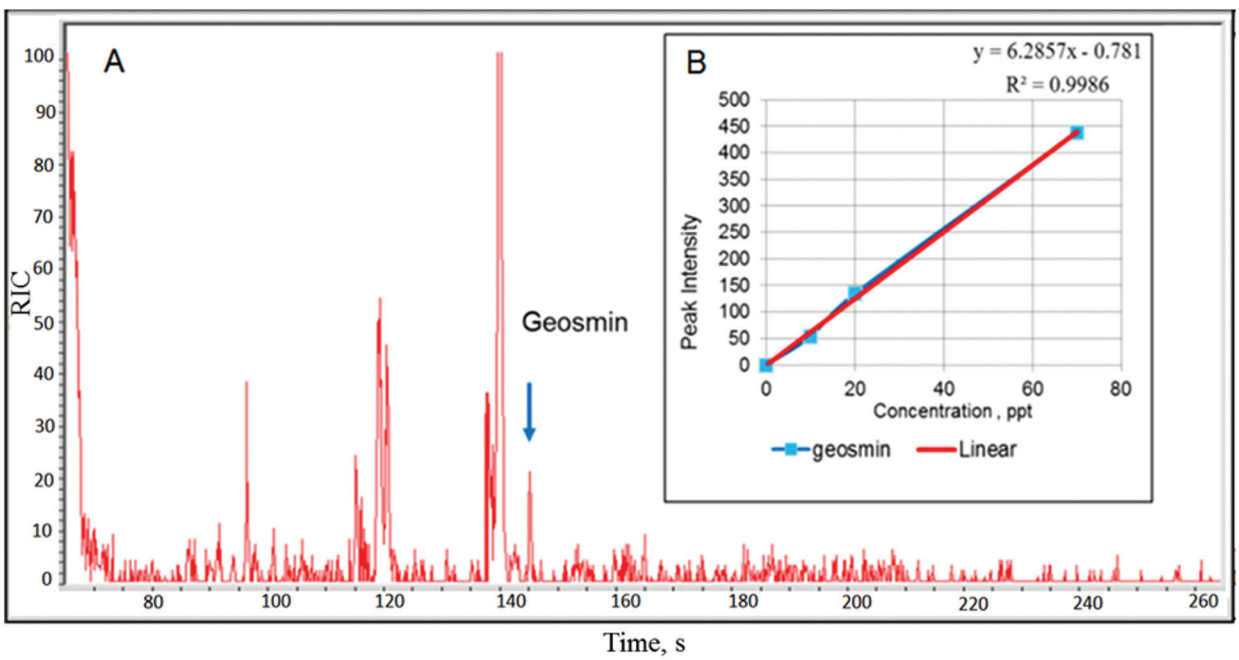


**Figure 7.** (A) Reconstructed-ion chromatogram (m/z 112) of 1 ppt geosmin (RSD ~ 10%) in 500 mL water extracted using a conventional SPE tube packed with PDMS and subsequently transferred to a needle trap before injection into the GC-MS system. SPE conditions: 500 mg, 125-180 µm PDMS particles; Needle trap conditions: 3 mg, 125-180 µm PDMS particles; GC conditions: 50 °C (10 s), 1 °C/s to 270 °C (10 s), 290 °C injector temp., 26 psi He pressure, 20 s splitless mode. (B) Calibration curve.

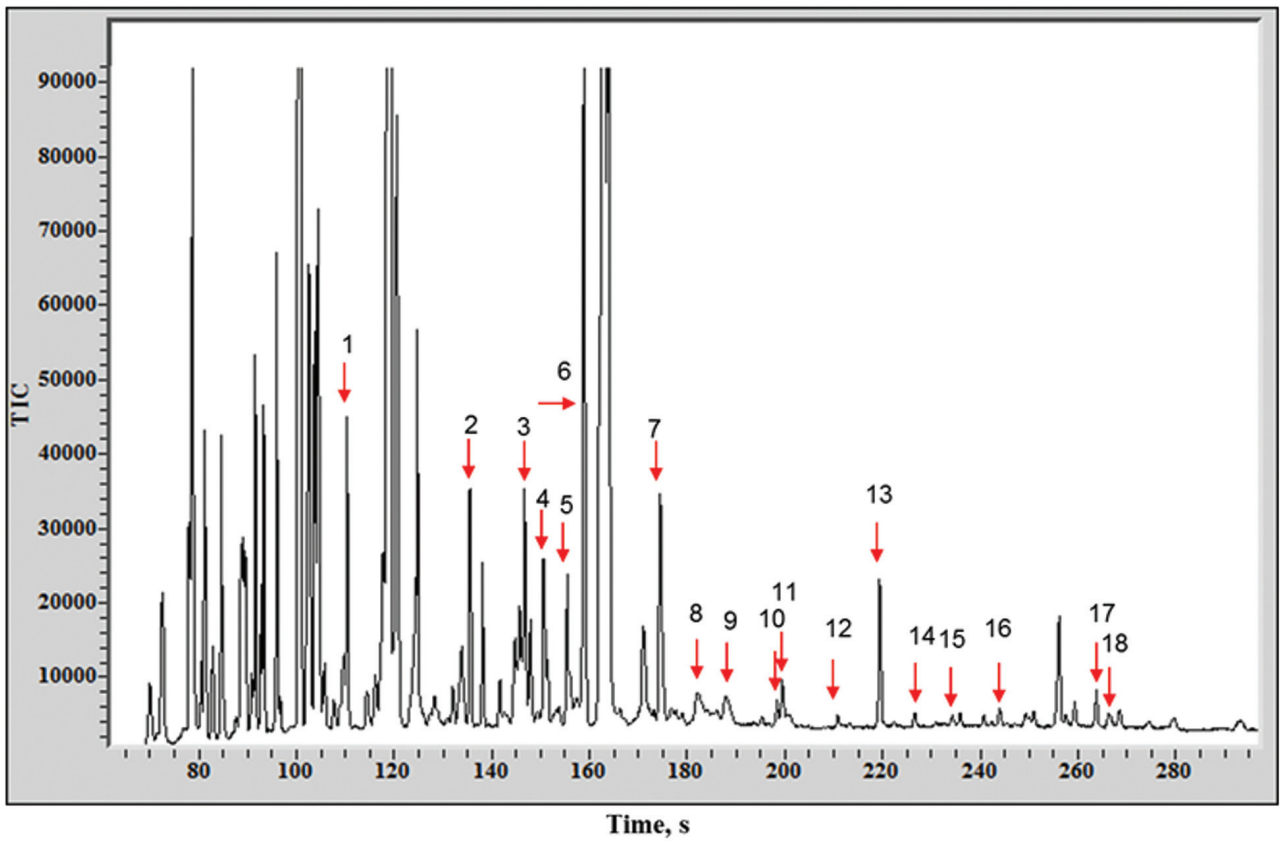


**Figure 8.** Total-ion chromatogram of 100 ppt (each component) PAHs and pesticides in water obtained using a combination of SPE and needle trap. SPE conditions: 500 mg, 125-180 µm PDMS particles; Needle trap conditions: 3 mg, 125-180 µm PDMS particles; GC conditions: 50 °C (10 s), 1 °C/s to 290 °C (10 s), 290 °C injector temp., He pressure: 26 psi, 20 s splitless mode. Peak identifications: (1) naphthalene, (2) 2-methylnaphthalene, (3) biphenyl, (4) 2,3-dimethyl naphthalene, (5) 2,6-dimethyl naphthalene, (6) acenaphthalene, (7) fluorene, (8) benfluralin, (9) lindan, (10) anthracene, (11) phenanthrene, (12) heptachlor, (13) chlorthal dimethyl, (14) heptachlor epoxide, (15) pyrene, (16) endrin, (17) methoxychlor, (18) chrysene.

0.1128 mg/mL by spiking 3.8 µL of dimethyl sulfide into 30 mL of methanol. Water samples were prepared by spiking 1 L of deionized water with varying amounts of the stock solution to provide concentrations of 0.5, 1.0, 2.0, 7.0 and 12.0 ppb. A 0.1 ppb standard was prepared by diluting the stock solution by10:1 and injecting 10 µL of this standard into 1 L of water. The simple purge-and-trap device that was used is illustrated in Figure 4B, and consists of a diaphragm vacuum pump, a purge vessel with air sparger and a needle trap. Following sample extraction, the needle trap was inserted into the GC-MS injection port where the target analytes were desorbed into a split-splitless injector (270 ºC). After an initial 30 s hold at 50 °C, the GC temperature was increased at 2 ºC/s to 120 ºC for a total run time of 65 s.

The external standard calibration curve was linear with an $R^2$ value of 0.9908. Figure 9 shows the results of analyses of dimethyl sulfide at 0.5 and 0.1 ppb in water. The practical detection limit for this method is estimated to be 0.15-0.20 ppb. The 0.1 ppb sample was detectable from the reconstructed-ion chromatogram; however, it could not be reliably identified using the automated quantitation software. It is reasonable to expect that lower detection limits could be achieved by further optimization of the method.

To prepare an air sample (5 ppb) for analysis, a 5 L Tedlar bag was spiked with 7.5 µL of 10:1 diluted dimethyl sulfide stock solution. The concentration was corrected for atmospheric pressure and temperature using US EPA method 10-2.4. Acetone partially co-elutes with

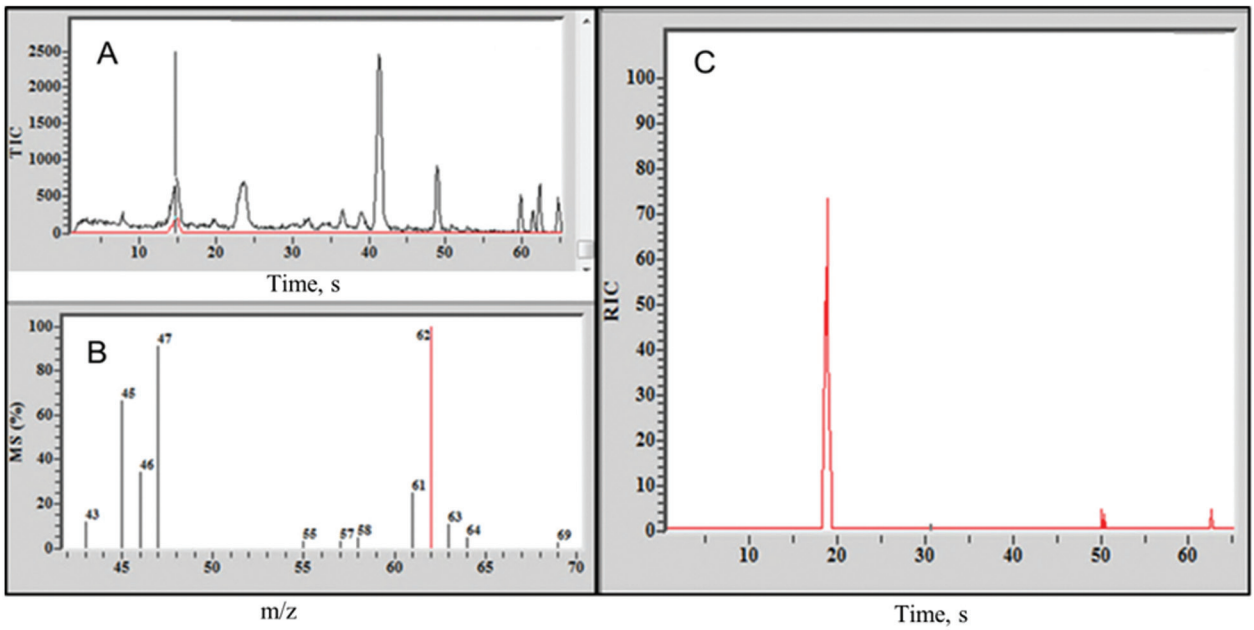


**Figure 9.** (A) Total-ion chromatogram and (B) mass spectrum of 0.5 ppb dimethyl sulfide in water; (C) extracted-ion chromatogram (m/z 62) of 0.1 ppb of dimethyl sulfide in water. GC conditions: initial temp: 50 °C (10 s), 2° C/s to 270 °C (10 s), 270 °C injector temp., 16 psi He pressure, 10:1 split mode.

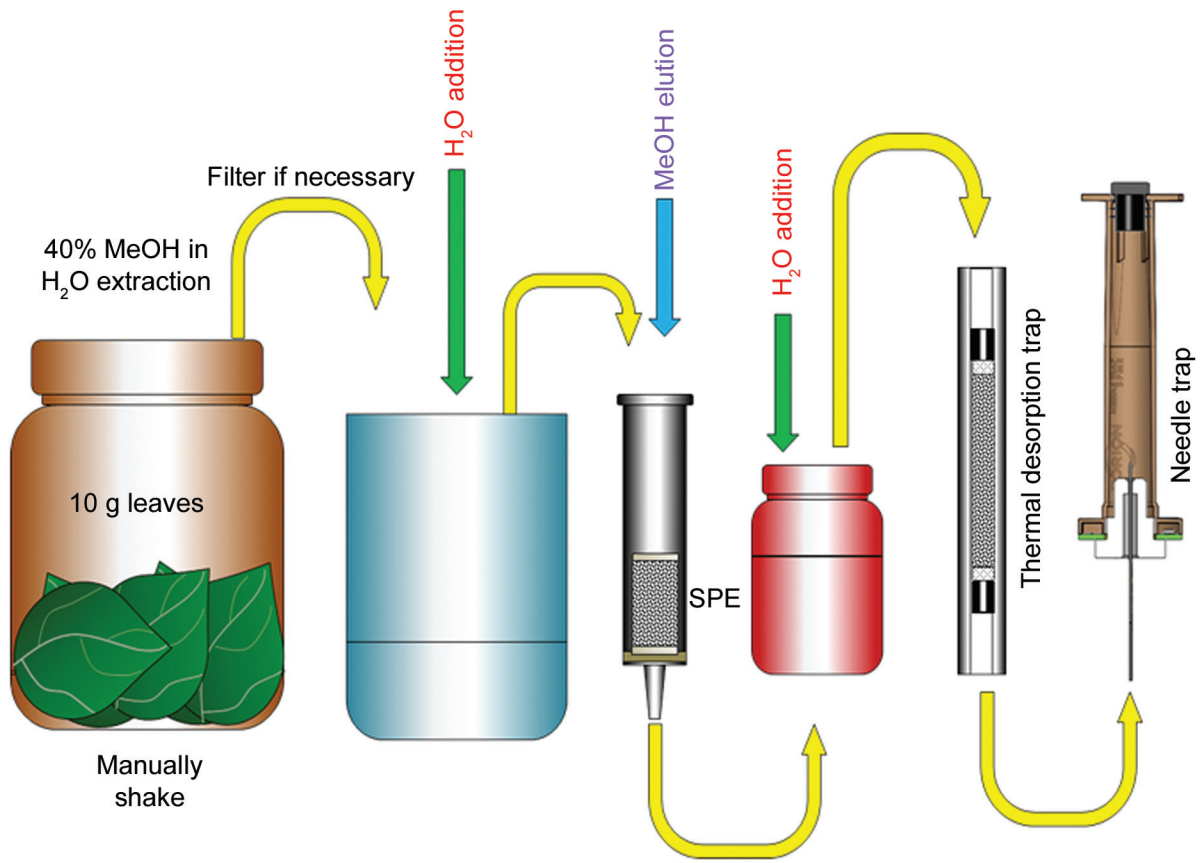


**Figure 10.** Diagram of the sample preparation procedure for analyzing pesticides in tea-like leaves.

**Table 2.** Retention times and characteristic m/z values used for GC-MS analysis of pesticides spiked on tea-like leaves.

| Name | RT, s | Ions, m/z |
|---|---|---|
| Dichlorvos | 134.5 | 109,185,79 |
| Mocap | 182.7 | 158,200,242,97,126,139 |
| Disulfoton | 204.1 | 88,274,97,60 |
| Methyl parathion | 212.8 | 109,125,263,79 |
| Heptachlor | 216.1 | 100,272,237,337 |
| Ronnel | 216.4 | 285,125,109,167 |
| Malathion | 219.7 | 173,125,93 |
| Metolachlor (Dual) | 222.7 | 162,238,146 |
| Dursban | 223.0 | 97,197,199,314 |
| Aldrin | 223.5 | 66,79,91,101,263,293,329,364 |
| Parathion | 223.7 | 291,109,97 |
| Heptachlor epoxide | 231.3 | 353,81,388 |
| p,p'-DDD olefine | 235.2 | 212,176,282,247 |
| Butachlor | 237.2 | 176,160,57,188,237,311 |
| endosulfan II | 238.2 | 195,241,277,339 |
| Tukuthion | 240.7 | 113,267,309,162,155 |
| p,p'-DDD | 242.3 | 235,165,199,320 |
| Dieldrin | 244.5 | 79,263,277,345,380 |
| Ethion | 250.5 | 231,384,153,97 |
| Carbofenothion | 255.3 | 157,342,199,97 |
| p,p'-DDT | 257.8 | 235,165,199,318,345 |

dimethyl sulfide, and a significant acetone background was present in the prepared air standard. However, the software was still able to extract and identify the dimethyl sulfide peak in the presence of acetone. Two hundred mL of air from the Tedlar bag spiked at 5 ppb dimethyl sulfide was sampled using the needle trap. The same chromatographic method was used as for the water samples. A concentration of 5 ppb dimethyl sulfide in air could be easily detected.

### 3.5. Detection of pesticides in fresh tea-like leaves

PDMS particles were again used for SPE of pesticide residues in fresh angiosperm tree leaves. Methanol and water were used as solvents, and a vacuum pump was used for drawing the headspace through the SPE and thermal desorption tubes. Analytes were again transferred by thermal desorption into a needle trap for transfer to the GC-MS. For sample treatment (see Figure 10), 10 g of the spiked leaf sample were extracted with 100 mL of methanol/water (40:60) in 3 subsequent portions (i.e., 40, 30 and 30 mL), and then with 2 additional portions of water (150 mL each).

**Table 3.** Recoveries of pesticides spiked on and extracted from tea-like leaves using SPE and thermal desorption transfer to a needle trap for GC-MS analysis.

| Name | Concentration, ppb | Recovery, % | Name | Concentration, ppb | Recovery, % |
|---|---|---|---|---|---|
| Carbophenothion | 50 | 113 | Endosulfan II | 19 | 103 |
| Ethion | 50 | 123 | Endosulfan sulfate | 55 | 69 |
| Malathion | 50 | 68 | Endrin | 20 | 124 |
| Parathion | 50 | 130 | Endrin aldehyde | 60 | 102 |
| Dichlorvos | 50 | 47 | Heptachlor | 9 | 71 |
| Disulfoton | 50 | 61 | Heptachlor epoxide | 9 | 87 |
| Dursban | 50 | 80 | *p,p'*-DDD | 57 | 85 |
| Guthion | 50 | 110 | *p,p'*-DDT | 18 | 56 |
| Methyl parathion | 50 | 98 | *p,p'*-DDE | 56 | 65 |
| Mocap | 50 | 91 | Alachlor | 50 | 117 |
| Ronnel | 50 | 69 | Atrazine | 50 | 66 |
| Tukothion | 50 | 49 | Bromacil | 50 | 128 |
| Aldrin | 10 | 78 | Butachlor and Alachlor | 50 | 91 |
| BHC isomer | 9 | 65 | Metolachlor | 50 | 70 |
| Dieldrin | 18 | 99 | Prometon | 50 | 92 |
| Endosulfan I | 19 | 96 | Simazine | 50 | 82 |

Filtering, salting out with sodium chloride and adjusting the pH were applied if necessary. SPE was carried out using 1 g of PDMS (125-180 µm particles) packed in a conventional 2 cm i.d. SPE tube. The sample was loaded at a flow rate of 40-60 mL/min. A washing step was performed with water (if salting out was applied). The elution step was performed with 10 mL of methanol (2 replicates, 5 mL each). The analytes were transferred to an SPE/thermal desorption tube at a flow rate of 15-20 mL/min after adding 90 mL of water. Then, they were desorbed and transferred to a needle trap at 275 ºC and 6 mL/min He carrier gas for 7 min using the FUZION desorber unit.

Tea-like leaf samples (10 g each) were spiked with standards (1-10 ppm) in methanol solution to produce ppb concentrations. The leaves were spiked by applying solution droplets using a 10 µL syringe on both surfaces. The solvent was allowed to evaporate completely in air for several hours. The leaves were then treated following the steps shown in Figure 10. GC-MS analysis gave low ppb semi-quantitative results (Table 2), which is sufficient for fast screening of fresh tea leaves in the field to help control the quality of the leaves before harvesting.

The recoveries of pesticides from the tea-like leaves were calculated based on the extracted-ion peak areas of the samples spiked with 32 pesticides at 10-60 ppb concentrations. Two standard samples and three leaf samples were evaluated. The average recoveries of the analytes are listed in Table 3, which varied from 64 to 128%.

### 3.6. Water elimination from the SPE tube containing PDMS particles

The presence of large amounts of water in the SPE sampling tube may affect the flow rate of the carrier gas in the thermal desorption step and, thus, the reproducibility of the procedure. Therefore, water must be eliminated before the thermal desorption step by applying a vacuum for approximately 3-5 min to the SPE tube after the sampling step is finished. A small amount of water present during transfer of sample to the needle trap did not affect the analytical results.

### 3.7. Protection of the hand-portable GC-MS system from contamination

The stability of the GC-MS system for long use depends on the cleanliness of the injected sample. Traditional liquid injection, although it is the most popular technique for GC analysis, is not the preferred choice for field GC-MS analysis because of a high probability of contamination from improper sample preparation and clean-up in the field. Alternatively, SPME and needle trap devices are ideal for sampling and concentrating target analytes from various sample matrices amenable to head space sampling, direct liquid extraction, purge-and-trap, and thermal desorption.

## 4. Conclusions

Trace analysis in the field using a hand-portable GC-MS is possible when using appropriate sampling and sample preparation methods. SPE, SPME, thermal desorption and needle trap methods have allowed the possibility of performing trace analysis in the field at ppb and ppt levels.

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# Porous polymer monoliths with incorporated single layer graphene

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**Abstract**

Single layer graphene has been used as an additive in poly(butyl methacrylate-*co*-ethylene dimethacrylate) monoliths. Incorporation of the carbon sheets into the polymer matrix was achieved by simple admixing graphene into the polymerization mixture containing both monomers and porogens. Chromatographic experiments indicated that some of the graphene layers were located at the pore surface and increased the apparent hydrophobicity of the material. Raman spectroscopy of the polymer containing graphene documented a rather homogeneous distribution of the single layer graphene sheets over wide areas of the monolith. However, the spectroscopy also confirmed the presence of other areas where the graphene sheets interacted with each other and formed clusters.

**Keywords:** Monolith; graphene; porous polymer; chromatography; Raman spectroscopy.

## 1. Introduction

The use of nanomaterials in separation science grew rapidly during the last decade because of their unique characteristics, which have been described in several excellent review articles[1-5]. Carbon-based nanostructures, an important member of the nanomaterials family, have been used in a variety of analytical applications. Nanotubes, fullerenes, nanodiamonds, and graphene have been used in applications such as sample preparation, separations, and detection[6-9]. For example, graphene and its oxidized counterpart were attached to capillary walls or immobilized onto polymer surfaces, and used in micro-extraction, gas chromatography, capillary electrochromatography, and liquid chromatography[10-19].

The unique porous structure of polymer-based monoliths makes them ideally suited for applications which require liquids to rapidly flow through the monolith with only a small amount of pressure, and/or where a fast mass transport is desired. These materials, which were introduced in the early 1990's, are now widely used in rapid chromatographic separations, and as excellent supports for immobilization of catalysts[20-29]. The introduction of carbon nanostructures, (mostly nanotubes and fullerenes), into the field of monoliths was spurred by the quest for improvements in their properties [17,30-33]. The arsenal of carbon nanostructures combined with monoliths was recently extended by the introduction of graphene and its derivatives because of their unique atomic structure, and their interesting electrical, mechanical and chemical properties. For example, Wang and Yan prepared monolithic capillary columns for electrochromatography in a single step by polymerizing a mixture of graphene oxide, methacrylic acid, ethylene dimethacrylate, cyclohexanol, and nitric acid[34]. Tong et al. added graphene nanosheets in a mixture of butyl methacrylate, ethylene dimethacrylate, 1-propanol, 1,4-butanediol, and azobisisobutyronitrile, and then polymerized the mixture in a capillary which produced a device for solid phase extraction of glucocorticoids[35]. Additionally, the same group prepared a poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) monolith in a capillary, modified it with ethylenediamine, and then attached graphene oxide to the free amine functionalities. This monolith was then used for the extraction of sarcosine from urine[36]. Recently, Li et al. reacted graphene oxide with 3-(trimethoxysilyl) propyl methacrylate, and then used the conjugate as a functional crosslinker which was added to a mixture of glycidyl methacrylate and ethylene dimethacrylate. This mixture was polymerized to form a monolithic capillary column designed for the separation of small molecules[37].

A major problem arising from all these approaches is the self-aggregation of the graphene. Due to van der Waals forces and electrostatic interactions, graphene tends to recombine and rebuild layered structures and aggregates from which it originated. Raman spectroscopy is a perfect tool to detect single layer graphene and to characterize the extent of this aggregation since the Raman shift relates directly to the number of graphene layers[38,39].

This communication describes the preparation of porous poly(butyl methacrylate-*co*-ethylene dimethacrylate) monoliths from polymerization mixtures including graphene, and for the first time shows the distribution of single layer and multilayer graphene in the monolith using Raman spectroscopy.

## 2. Experimental section

### 2.1. Chemicals and Materials

Monomers, butyl methacrylate and ethylene dimethacrylate, porogenic solvents, 1,4-butanediol and 1-propanol, initiator azobisisobutyronitrile (AIBN), trifluoroacetic acid, 3-(trimethoxysilyl) propyl methacrylate, benzene and ethyl benzene were purchased from Sigma-Aldrich (St. Louis, MO, USA). The monomers were passed through basic aluminum oxide placed in a column to remove the inhibitors. HPLC-grade solvents acetonitrile, acetone, methanol and ethanol were purchased from EMD Chemicals Inc. (Gibbstown, NJ, USA). Single layer graphene powder was purchased from ACS Material LLC (Medford,

MA, USA). All chemicals were of the highest quality available. Polyimide coated 100 μm i.d. fused silica capillaries were purchased from Polymicro Technologies (Phoenix, AZ, USA).

### 2.2. Preparation of monoliths

The inner surface of the fused silica capillary was "vinylized" with 3-(trimethoxysilyl)propyl methacrylate using a procedure described in detail elsewhere[31] to enable covalent attachment of the monolith. The polymerization mixture for the generic capillary columns consisted of 23.4 wt% 1,4-butanediol and 36.6 wt% 1-propanol, 24.0 wt% butyl methacrylate and 16.0 wt% ethylene dimethacrylate, and AIBN (1 wt% with respect to monomers). In some cases, the single layer graphene powder (0.25 wt% with respect to monomers) was added to the polymerization mixture. The polymerization mixture was homogenized by sonication for 10 min and degassed by purging with nitrogen for 5 min before it was pushed into the vinylized capillary. Both ends of the filled capillary were sealed with a rubber septum, and then the capillary was submerged in a termostated water bath. After completion of the polymerization at 70 °C for 24 h, a piece was cut from both ends of the capillary, the monolith was flushed with acetonitrile to remove the unreacted components, and characterized. The remaining polymerization mixture was polymerized in a glass vial at 70 °C for 24 h, to obtain the bulk material. This monolith was purified with methanol using a Soxhlet extractor and dried in a vacuum oven.

### 2.3. Instrumentation

Scanning electron micrographs were obtained using a Zeiss Gemini Ultra Field-Emission Scanning Electron Microscope (Peabody, MA, USA). The samples were sputtered with gold using the SCD 050 sputter coater (BAL-TEC AG, Balzers, Lichtenstein). Raman spectra and maps were obtained using a confocal LabRAM Raman microscope from Horiba Jobin Yvon (Edison, NJ, USA). A 1200 series nano flow HPLC system from Agilent Technologies (Santa Clara, CA, USA) consisting of a degasser, a 80 nL UV detection flow cell, and an external microvalve injector with a 10 nL sample loop (Valco Instruments Co Inc., Schenkon, Switzerland) were used for the chromatographic tests. Separation of acetone, benzene, and ethyl benzene was carried out at a flow rate of 2 μL/min using the mobile phase consisting of water and acetonitrile (50/50, v/v). The injection volume was 10 nL and the detection wavelength 210 nm.

## 3. Results and discussion

### 3.1. Preparation of methacrylate monoliths containing graphene

The preparation of monolithic columns using butyl methacrylate and ethylene dimethacrylate as monomers has previously been optimized and reported by our group[40]. In the subject experiments we applied this approach to the preparation of monoliths containing graphene. To do so, we first chose to admix the commercial single layer graphene directly into the monomer mixture. To our disappointment, we observed the aggregation of graphene and the formation of a rapidly sedimenting black powder when we added the pristine powder to the mixture containing only both monomers. This result was most likely caused by the highly hydrophobic nature of the graphene itself and its tendency to reform back to the original graphite structure. However, the presence of porogenic solvents, 1-propanol and 1,4-butandiol, in the solution prevented the precipitation. These solvents appear to act as a surfactant and the more protic environment decreases the tendency of graphene to self-aggregate. Vigorous mixing and sonication led to a stable homogeneous black dispersion.

Figure 1 compares SEM images of the original poly(butyl methacrylate-*co*-ethylene dimethacrylate) monolith and its counterpart containing 0.25 wt% graphene, which was the maximum that could be homogeneously dispersed. The polymerization in the presence of the graphene produced a monolith with a changed morphology, and leads to an increase in the size of the through pores. The significant difference in the polymer surface and the dramatically changed structure was clearly visible in images obtained using a larger magnification.

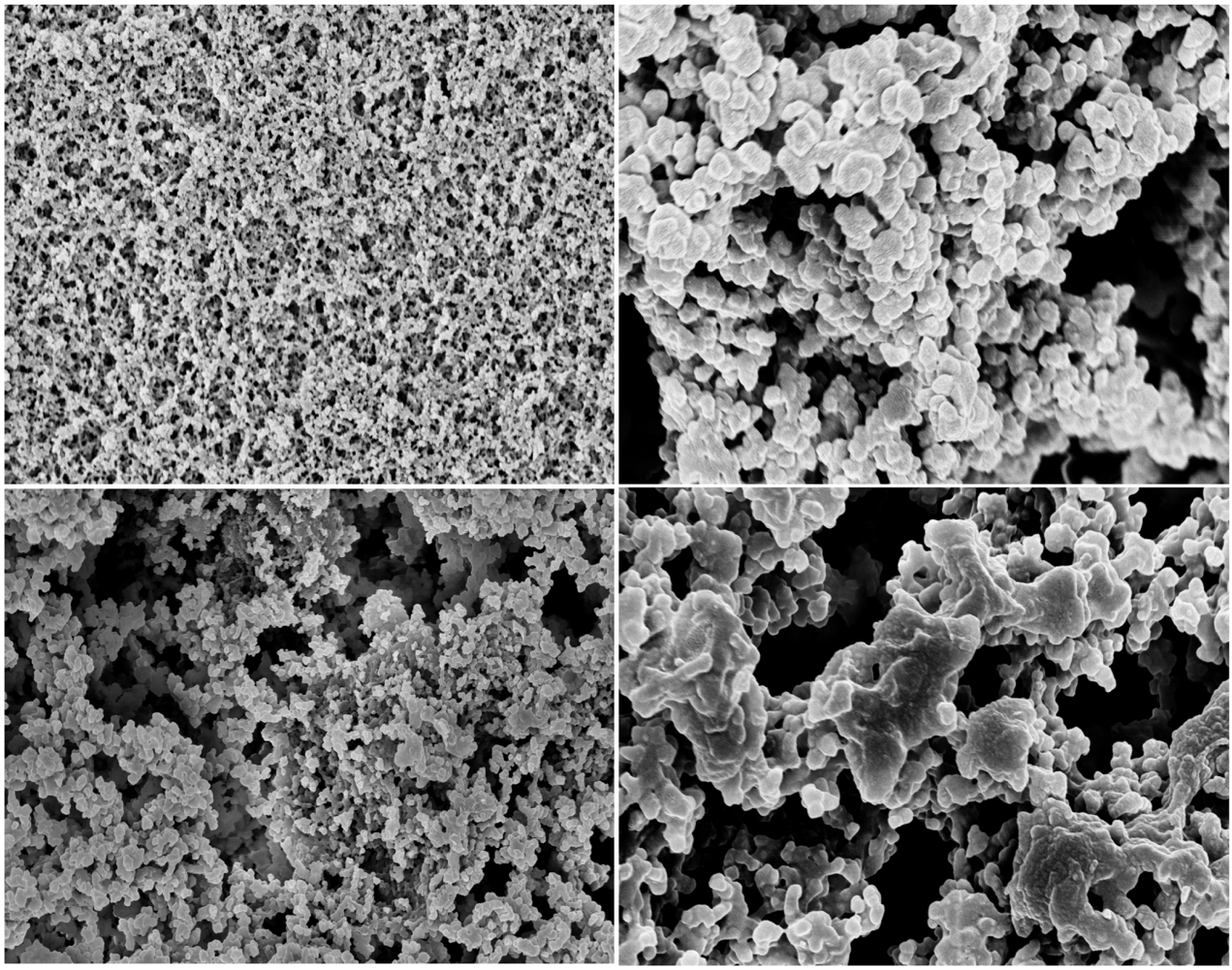

**Figure 1.** SEM images of poly(butyl methacrylate-*co*-ethylene dimethacrylate)monolith (top) and its counterpart prepared from a polymerization mixture containing 0.25 wt% graphene flakes (bottom).

Interestingly, this change in morphology was not reflected in the changes in surface area of the monoliths. Both the white-colored poly(butyl methacrylate-*co*-ethylene dimethacrylate) monolith and the grayish monolith containing graphene had surface areas of 14 $m^2/g$. We speculate that this resulted from the small amount of graphene that was added, which even under the best scenario, was not attached perpendicularly to the pore surface. Instead, laied flat and covered the pore surface. As a result, the graphene did not contribute to any increase in the surface area.

Chromatographic experiments provided another piece of evidence indicating the presence of graphene at the pore surface. We used both parent poly(butyl methacrylate-*co*-ethylene dimethacrylate) monolithic capillary columns and its graphene-containing counterpart to separate a mixture of acetone, benzene and ethyl benzene in reversed phase mode. The resulting chromatograms are presented in Figure 2. No separation was achieved using the parent column and only a single broad peak was obtained. In contrast, the presence of a very small amount of graphene increased retention of hydrophobic benzene derivatives and enabled separation of all three compounds. The column efficiency was not very high due to the very small surface area. However, this result clearly indicates that at least part of the graphene was located at the pore surface.

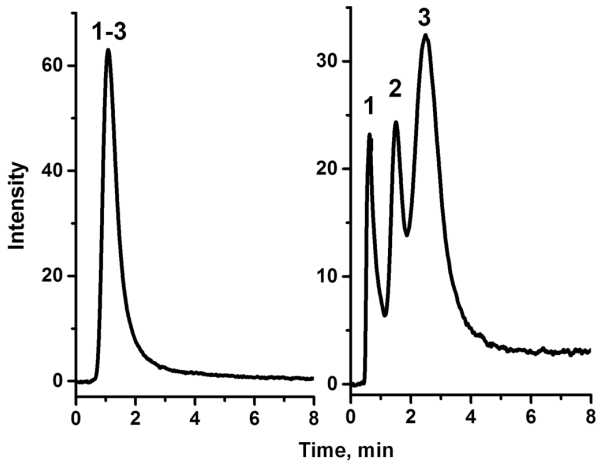


**Figure 2.** Separation of acetone (1), benzene (2) and ethyl benzene (3) using monolithic poly(butyl methacrylate-*co*-ethylene dimethacrylate) capillary column (A) and its counterpart containing 0.25 wt% (B) entrapped graphene flakes Conditions: Column 10 cm x 100 µm i.d., mobile phase 50:50 vol% acetonitrile- water, flow rate 2.0 µL/min, injection volume 10 nL, UV detection at 210 nm.

### 3.2. Raman spectroscopy

While the incorporation and possible re-arrangement of the graphene layers into clusters with a graphite-like structure is likely, direct evidence is needed to describe the distribution of the carbonaceous compounds within the monolith. Raman spectroscopy is a simple standard technique for the characterization of $sp^2$ and $sp^3$ hybridized carbon atoms in different forms of carbon such as fullerene, graphite, and graphene[38]. In this work Raman spectroscopy was used to investigate the distribution of graphene in both the monoliths prepared in bulk, and in the capillary columns.

First, an argon laser was used with an excitation wavelength of 488 nm that provided spectra with a good resolution. However, the significant background photoluminescence made their interpretation difficult. Therefore, a 532 nm laser was subsequently used to obtain maps with good spatial information. Unfortunately, a broad peak originating from the monolith was present in the range around 2700 $cm^{-1}$, which was also characteristic for the *2D* peak of graphite and graphene. Therefore, we had to utilize the *G* peak to identify the distribution of graphene in the monolith. Wang et al. found that the wavenumber of the *G* peak for graphene and graphite depends on the number of their layers and shifts toward lower wavenumbers with the increase in the number of layers[41]. The spectrum of the monolithic column containing graphene (shown in Figure 3) exhibits a small split in the *G* peak, most likely representing self-ordering of the graphene layers during or after the preparation of the monolith.

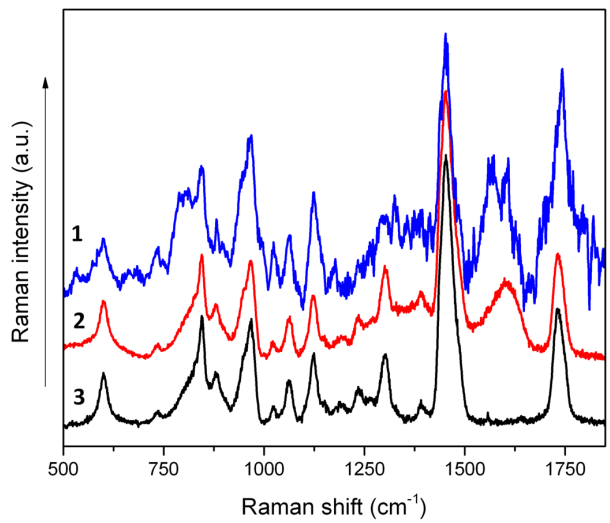


**Figure 3.** Raman spectra of the bulk monolithic material (3), bulk monolithic material with incorporated graphene (2), and monolith containing graphene in capillary (1).

The excitation wavelength of 532 nm was first utilized to find locations of the *G* peaks for commercial graphite and graphene flakes. The Raman shifts occurred at 1577 $cm^{-1}$ and 1604 $cm^{-1}$, respectively, and were used to map the distribution of the graphene in the bulk sample. Spectra for the map in Figure 4 were taken every 2 µm and the peak intensity in the different regions was integrated. The white color intensity in the left map refers to the disordered region, which contained the multi-layer graphene or graphite. The map on the right indicates the distribution of graphene which was present in a single-layer or clusters of only a few layers. The images indicate that some of the originally single layer graphene flakes partially reordered during the preparation of the monolithic structure. This process resulted in formation

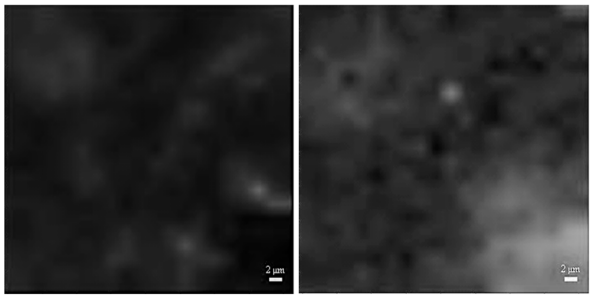

**Figure 4.** Raman map depicting the distribution of graphene and graphite obtained from the G-band. White color corresponds to the peak intensity 1570-1585 $cm^{-1}$, i.e. the graphite region (left) and between 1590-1615 $cm^{-1}$ characterizing the graphene region (right).

of disordered regions where graphene layers were located at a distance allowing their interactions with each other. However, and more importantly, this spectral study also confirmed that the graphene monoliths retained a significant amount of graphene in the single layer form since more white spots were seen in the right panel than in the left one.

## 4. Conclusion

This study demonstrated that poly(butyl methacrylate-*co*-ethylene dimethacrylate) monoliths can be successfully doped/modified with single layer of graphene by its inclusion in the complete polymerization mixture. A significant proportion of the graphene appeared to be incorporated in the polymeric structure in the form of single layers. The increase in hydrophobic interactions indicates that at least a part of graphene was located at the pore surface. Further work will focus on the preparation of monoliths with a greater percentage of graphene and its homogeneous distribution in the polymer. In order to improve the chromatographic performance, monolithic columns with much larger surface areas will be prepared with their surface area increased using the hypercrosslinking reaction.

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# Development of a dynamic headspace – capillary GC – MS method for the determination of ultra-trace levels of vinyl chloride in water samples and during migration studies

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**Abstract**

A method based on automated dynamic headspace sampling followed by thermal desorption – capillary GC – MS was developed to monitor ultra-traces of vinyl chloride in water samples. The method shows excellent performance including a limit of quantification (LOQ) below 10 ng/L, good linearity (r2 > 0.999) in the 10 to 200 ng/L concentration range and an RSD below 10% at all calibration levels. The method was applied to study the release of traces of vinyl chloride monomer (VCM) in water from aged polyvinyl chloride (PVC) pipes installed in water supply systems. A solution to avoid this leaching would be the insertion of a polyethylene pipe inside the PVC pipe provided that vinyl chloride does not permeate through polyethylene. Vinyl chloride migration through a high density polyethylene (HDPE) film was therefore studied with the developed sampling method.

**Keywords:** Vinyl chloride, Dynamic headspace, Capillary GC – MS, Migration, Polyethylene film.

*Paper dedicated to Professor Harold McNair, a very loyal friend and outstanding colleague.*

## 1. Introduction

Whatever its synthesis process, polyvinyl chloride (PVC) intrinsically contains residual vinyl chloride (VCM or vinyl chloride monomer)[1]. After confirmation of the toxicity of VCM in 1974, PVC manufacturers optimised their production processes to reduce VCM concentrations in PVC from 200 mg/kg in the early 70's to less than 1 mg/kg in recently manufactured PVC products.

Through leaching and migration, VCM is a potential contaminant for the environment and water supplies, which might raise health issues since vinyl chloride is classified as a group 1 carcinogen[2]. The concentration of vinyl chloride that can potentially migrate out of polyvinyl chloride pipes into water is mainly dependent on the concentration of residual VCM in the used PVC material[3,4,5]. Moreover, Al-Malack et al.[6,7] demonstrated that the vinyl chloride release from PVC pipes is also influenced by temperature, pH, total dissolved solids and solar irradiation. An EU Directive specifies that polymers that might come in contact with food products should not contain VCM levels above 1 mg/kg and that the vinyl chloride content in food products should be below 10 µg/kg[8]. More recently, the World Health Organization (WHO) set a maximum residue level of 300 ng/L (0.3 ppb) vinyl chloride in drinking water[2].

As vinyl chloride is gaseous at ambient conditions, the analytical technique of choice is gas chromatography (GC). A limit of detection in the order of 1 µg/L could be reached for the determination of vinyl chloride in water samples by static headspace sampling in combination with GC – MS[6,7,9,10]. Higher sensitivities were obtained using purge and trap (P&T) sampling[11,12]. US-EPA method 524.2 describes the analysis of more than 60 volatile organic compounds (VOCs) including VCM by P&T – GC – MS[13]. The detection limit for vinyl chloride in water is 40 ng/L. Other detectors such as electron capture detection (ECD)[14] and electrolytic conductivity detection (ELCD)[15] were used in P&T – GC and detectabilities were in the order of 40-100 ng/L. Direct aqueous injection in combination with GC – MS was also applied to VCM determinations with LODs of 100 ng/L[16]. However, the use of cool on-column injection is mandatory making this method not applicable to samples containing high levels of non-volatile material such as salts. Solid phase micro-extraction (SPME)[17-19] and headspace solid-phase dynamic extraction (HS-SPDE)[20] were also applied for VCM determinations but LODs were higher than with P&T.

To our knowledge, the highest analytical sensitivity reported for VCM (LOD of 1.6 ng/L) was obtained by combining off-line P&T followed by derivatization of VCM into 1,2-dibromo-chloroethane and GC – ECD analysis[21-23]. This methodology is, however, difficult to apply in routine analysis and the on-line P&T – GC – MS is preferred to monitor VCM according to the WHO guideline.

In our studies on migration kinetics, higher sensitivities were needed and therefore another analytical method was developed. One of the major problems with P&T is the presence of water on the trap. In P&T, an inert gas is bubbled through the aqueous sample and a substantial amount of water is also transferred into the trap and/or analytical system. Increasing sample temperature, extraction time and flow are beneficial for the extraction efficiency of most VOCs, but also increase the amount of "purged" water. Although several water management systems are available for P&T e.g. Nafion dryers[11], water is still interfering with vinyl chloride detection in GC.

For this reason, dynamic headspace sampling (DHS), whereby the water is not purged, but only the gaseous headspace is flushed with an inert gas, was applied as alternative. DHS is performed on a modified XYZ robot developed and commercially available for liquid injection, static headspace sampling and solid phase micro-extraction, resulting in a very flexible multi-purpose sampler. The dynamic headspace adaptor allows to purge the headspace of the sample placed in a 20 mL

vial under controlled temperature and flow conditions. The VOCs are trapped on an exchangeable packed trap (e.g. Tenax, charcoal) at a precise temperature. Finally, the VOCs are thermally desorbed (TD) and analyzed. After optimization of the operational parameters, the dynamic headspace method was applied to evaluate migration of vinyl chloride through a polyethylene thin film.

## 2. Experimental

### 2.1. Chemicals and sample preparation

Vinyl chloride monomer (VCM) was obtained as a concentrated solution in methanol (2,000 µg/mL) from Supelco (Sigma-Aldrich, Bellefonte, USA). Dilutions at 0.1 and 1 µg/mL were prepared in methanol (headspace analytical grade, Sigma-Aldrich). Deuterated vinyl chloride (VCM-d3) was obtained from Cambridge Isotope Laboratories (LGC Standards, Molsheim, France) as a 50 µg/mL solution in deuterated methanol. A diluted solution at 0.5 µg/mL in methanol was used as internal standard (IS).

Method validation was done using bottled drinking water (Vittel). Aliquots of 10 mL were spiked with 1, 2 or 5 µL of the 0.1 µg/mL and 1, or 2 µL of the 1 µg/mL VCM standards to obtain calibration samples at 10, 20, 50, 100 and 200 ng/L level. From the IS solution, 4 µL was added, resulting in a 200 ng/L IS level.

### 2.2. Instrumental conditions

An automated dynamic headspace system (DHS) installed on an MPS2/TDU unit (Gerstel GmbH, Mülheim an der Ruhr, Germany) in combination with a 7890GC – 5975MSD (Agilent Technologies, Wilmington, USA) system was used. The principle of operation is illustrated in Figure 1. During DHS, the sample headspace (10 mL) is purged at 10 °C during 6 min with a flow of 50 mL/min helium (total purge volume = 300 mL) while the vial is agitated. The purged solutes are trapped at 15 °C on a mixed bed composed of Carbotrap B, Carbotrap X and Carbosieve 1000 (B-X-1000 adsorbent from Gerstel GmbH), placed in a TDU (thermal desorption unit) liner.

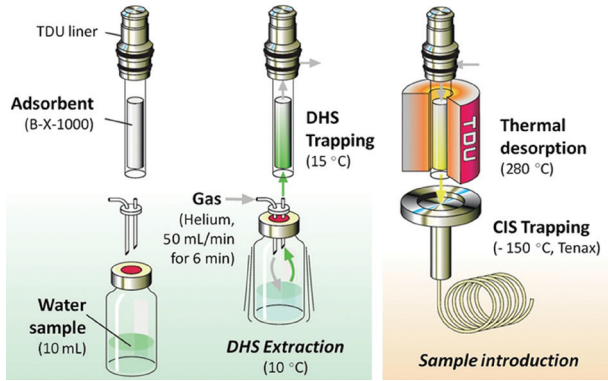


**Figure 1.** Principle of dynamic headspace sampling for VCM in water samples.

After dynamic headspace extraction, the trap is desorbed at 280 °C during 5 min and the released solutes are cryo-focussed in a programmable temperature vaporizer (PTV – CIS-4, Gerstel) interface operated at –150 °C in the splitless mode using a Tenax packed liner. Finally, the CIS-4 is programmed to 280 °C (7 min hold) for injection in split (1/10) mode.

Separation was done on a 60 m x 0.25 mm x 1.4 µm DB-624 column (Agilent Technologies) using helium as carrier gas at 1.5 mL/min constant flow (160 kPa at 35 °C). The GC oven was programmed from 35 °C (1 min) at 5 °C/min to 60 °C and at 25 °C/min to 250 °C (0.4 min). Mass spectrometric detection was done in SIM mode using ions at 62 and 64 for VCM and ions 65 and 67 for VCM-d3 (IS). Dwell times were 75 ms for each ion. Electron ionization at 230 °C source temperature was used. Quantification was done using the ions at m/z 64 and 67, since they resulted in higher selectivity than the more abundant ions at m/z 62 and 65. The latter ions were used for confirmation.

### 2.3. Migration study

To evaluate VCM migration through a polyethylene thin film, the experimental set-up shown in Figure 2 was used. Basically, a glass U-tube was designed to place a thin (355 µm) film of high density polyethylene (HDPE) in the middle of the device. The film was tightened between two junctions. On both sides of the U-tube 250 mL water was introduced.

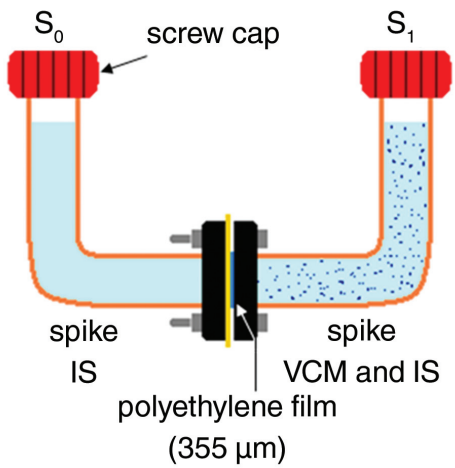


**Figure 2.** Experimental set-up for determination of vinyl chloride migration through polyethylene.

To test vinyl chloride migration, 150 µL of a 10 µg/mL solution of VCM in methanol was spiked at the $S_1$ side of the device resulting in 6 µg/L (ppb) spiking level. Internal standard (100 µL from 0.5 ppm solution in methanol) was added to the $S_1$ and $S_0$ side. The small amount of methanol relative to the water amount (250 mL) was considered as having no influence on migration. Sampling of 10 mL was performed on the $S_0$ side before spiking (t-1, blank check), immediately after spiking and homogenization (t0), and after 1 (t1), 2 (t2), 3 (t3), 4 (t4) and 7 (t7) days. The samples were placed in 20 mL headspace vials and analyzed as described for the water samples.

## 3. Results and discussion

### 3.1. Dynamic headspace method development

Vinyl chloride is very volatile and optimum sampling conditions were found to be different from standard conditions used for static headspace or P&T analysis of VOCs such as benzene, toluene or xylene. On the other hand, in generic VOC analysis applying headspace methods, salt is often added to decrease the water solubility of the solutes and increase the solute concentration in the headspace ("salting out"). Salt addition was not applied as it was observed that this resulted in sample heating and loss of VCM.

Performance of the DHS method for VCM analysis is dependent on different parameters, including purge conditions (flow × time), sample temperature, solute trapping (adsorbent type and temperature) and desorption conditions. These parameters were varied and their influence on peak shape, peak area (sensitivity) and repeatability was evaluated.

A purge flow of 50 mL/min during 6 min was found to be sufficient for a 10 mL sample volume. A second dynamic headspace extraction performed on the same sample, showed that quantitative extraction was obtained by flushing 30 times the headspace volume (10 mL). Longer purge times and/or higher flow rates resulted in breakthrough of vinyl chloride through the DHS trap. The highest recovery, and thus highest sensitivity, was obtained on a B-X-1000 three bed trap (Carbotrap B, Carbotrap X and Carbosieve 1000). This trap performed much better than a standard Tenax trap. A trap temperature of 15 °C was optimum. Higher trap temperatures resulted in loss by breakthrough of VCM.

An important parameter was the sample temperature (dynamic headspace incubator). Elevated temperatures (up to 70-85 °C) are often used in generic headspace methods, but the best results for vinyl chloride were obtained at low sample equilibrium temperatures. This is commensurate with the observations made by Hino et al.[24]. At relatively low sample temperature (10 °C), extraction is complete and apparently it also influences trapping efficiency, desorption and GC – MS analysis, since less water is transferred to the trap and further to the column and detector. Keeping all parameters constant, the peak area of VCM was ca. 2 times higher at 10 °C equilibrium temperature compared to 20 °C. The best peak shape and highest peak area for VCM were obtained when the CIS-4 inlet was placed at -150°C and the liner packed with Tenax. The other desorption conditions listed in the experimental section were found to result in quantitative desorption/injection of VCM. Moreover, no carry-over was noted during a second desorption of the trap. Figure 3 shows the analysis of a water sample spiked with 10 ng/L VCM and 200 ng/L VCM-d3 internal standard.

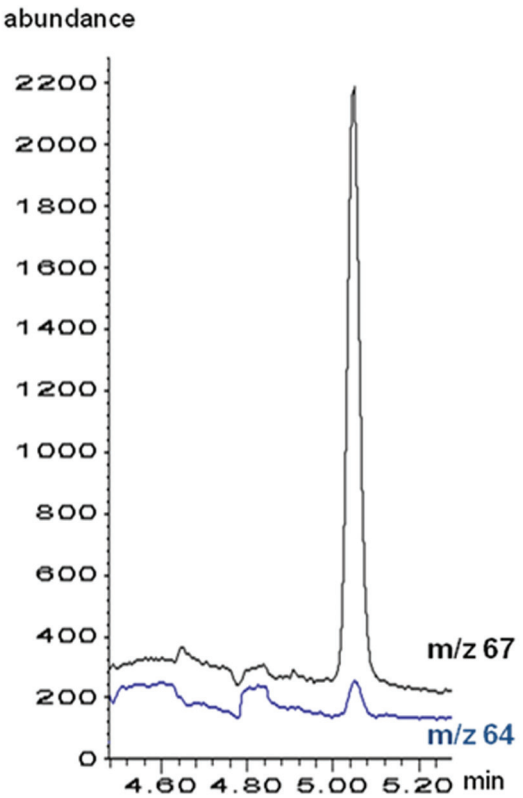


**Figure 3.** Extracted ion chromatograms of the DHS – TD – GC – MS analysis of VCM (ion m/z 64) and internal standard (d3-vinyl chloride, m/z 67) in a water sample spiked at 10 ng/L (VCM) and 200 ng/L (IS).

**Table 1.** Figures of merit for VCM determinations using DHS – TD – GC – MS.

| Parameter | Concentration level or range | Performance |
|---|---|---|
| Linearity | 10 – 200 ng/L | $R^2$ = 0.9996 |
| RSD % (n = 6) | 10 ng/L | 8.2 % |
| RSD % (n = 6) | 50 ng/L | 7.1 % |
| RSD % (n = 6) | 200 ng/L | 9.9 % |
| S/N | 10 ng/L | 13.6 |
| LOD (S/N = 3) | | 2.2 ng/L |
| LOQ (S/N = 10) | | 7.3 ng/L |

**Table 2.** Measured VCM concentration (ng/L) in $S_0$ as a function of time for a 6 µg/L level spiking in $S_1$ (see Figure 2).

| Time (days) | 6 µg/L | | |
|---|---|---|---|
| | Sample 1 | Sample 2 | Average |
| -1 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 |
| 1 | 2 | 2 | 2 |
| 2 | 7 | 11 | 9 |
| 3 | 19 | 22 | 20,5 |
| 4 | 47 | 35 | 41 |
| 7 | 65 | 55 | 60 |

### 3.2. Method validation

Some figures of merit are presented in Table 1. The linearity in the concentration range between 10 ng/L and 200 ng/L is excellent with RSDs below 10% at all calibration levels. The signal-to-noise ratio, determined using peak-to-peak noise, on the extracted ion chromatogram for m/z 64 from the analysis of a water sample spiked at 10 ng/L was 13.6. From this, a limit of detection (LOD) of 2.2 ng/L (S/N = 3) and a limit of quantification (LOQ) of 7.3 ng/L (S/N = 10) were calculated. These values are in the same order as those reported for the off-line P&T – derivatisation – GC-ECD method of Wittsiepe et al.[21-23].

### 3.3. VCM migration through a thin film of polyethylene

The migration test was performed in duplicate at the concentration level of 6 µg/L in $S_1$ (Figure 2). The results are given in Table 2. First of all, it can be observed that the duplicates give close results illustrating the repeatability of the determination. In addition, it is obvious that the high sensitivity of the method is required to detect VCM migration. Note that at t1 the concentration is close to the LOD value and at t2 close to the LOQ value. The concentration of VCM in the non-spiked side ($S_0$) increased from 2 to 60 ppt within 7 days. From this experiment, it is clear that vinyl chloride migrates through the HDPE thin film. By plotting the vinyl chloride migration value as a function of time, a linear curve was obtained for the first 3 days (72 h). This curve was used for the determination of the VCM diffusion coefficient.

The diffusion of a solute through a film is described by Fick's Law:

$$\frac{dQ}{dt} = -D.A.\frac{dC}{dx} \quad (1)$$

where by dQ/dt is the flux of molecules that pass the membrane in function of time (mol/s), D is the diffusion coefficient (cm²/s), A is the membrane area (cm²) and dC/dx is the concentration gradient (with dC in mol/cm³ and dx in cm). By plotting the concentration (in nmol) as a function of time (in hours), the curve concentration (nmol) = 0.0016 time (hours) - 0.0153 ($R^2$ = 0.9194) was obtained by linear regression, using the data points between 0 and 72 h (3 days).

Using the experimental data, the diffusion coefficient D was calculated using:

$$-D = \frac{dC}{dt}.\frac{1}{A}.\frac{d}{C_0} \quad (2)$$

in which dC/dt is the slope of experimental curve of concentration (nmol) increase as a function of time (hours), A is 28.27 cm² (diameter of membrane exposed = 6 cm), d is the film thickness (355 µm or 0.0355 cm) and $C_0$ is the concentration of vinyl chloride at spiked side (80 nmol/L). The calculated diffusion coefficient is 2.51 E-05 cm²/hour.

The experiment was repeated for a 60 µg/L concentration and the diffusion coefficient was 2.06 E-05 cm²/hour. The obtained values are close and the average diffusion coefficient for vinyl chloride migration through a polyethylene film (at room temperature) is thus in the order of 2.3 E-05 cm²/hour or 5.5 E-08 m²/day. The diffusion coefficient is at present refined by additional tests on several HDPE film thicknesses and VCM concentrations. Such data are of great value for engineering purposes of drinking water pipeline networks.

## 4. Conclusion

Sensitive and reliable determination of vinyl chloride in water samples could be achieved using dynamic headspace combined with thermal desorption – GC – MS. Using a relatively low extraction temperature and optimized DHS and thermal desorption parameters, the limit of quantification is below 10 ng/L. This innovative method has been implemented to assess vinyl chloride migration through polyethylene films.

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SAMPLE PREPARATION

# Supercritical fluid extraction followed by gas chromatography-mass spectrometry determination of electrical-grade insulating oil residues from activated bauxite

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**Abstract**

The electrical-grade insulating oils widely used in high-voltage power equipment produce degradation by-products during their service life. Filtering the aged oil through an adsorbent material such as activated bauxite usually eliminates such by-products. As a consequence the adsorbent will be contaminated with several chemical species thus hindering its direct discharge in the environment. In the present work, a methodology was developed and optimized to extract oil residues adsorbed in activated bauxite by dynamic supercritical fluid extraction (DYN-SFE) employing $CO_2$ as extraction solvent. Characterizing the extracted residues by GC-MS allowed following the remediation process, showing that the developed method was effective in extracting the vast majority of the compounds detected in the insulating oil studied. However, the extraction of carboxylic acids from oil degradation requires to be optimized in a future study.

**Keywords:** SFE; GC-MS; insulating oil; activated bauxite; remediation; $CO_2$.

*Dedicated to Professor Harold McNair on the occasion of his 80th birthday.*

## 1. Introduction

Electrical-grade insulating oils have been widely used as an insulating fluid and a heat exchange medium since 1890. Such an application is concentrated in the most apparatuses installed on electric power transmission and distribution systems. In order to perform its task, insulating oils must maintain the dielectric strength and the heat dissipation characteristics when used in power transformers[1].

The insulating oil is frequently called mineral oil to differentiate it from vegetable and animal oils since it is manufactured from crude petroleum, which is geologically classified as a rock. The crude oil is distilled and separated in distinctly different commercial fractions from which several industrial products are obtained. The fraction separated in distillation towers at temperatures between 300-400°C is employed in the production of insulating oils[2].

An insulating oil is composed basically by aliphatic, cycloaliphatic and mono-, di-, tri- and polycyclic aromatic hydrocarbons. A minimum amount of compounds containing sulphur, nitrogen and oxygen atoms can also be found.

Oil molecules oxidize in the presence of oxygen and metallic catalysts when heated at a high temperature (e.g. 100°C)[3]. A series of reactions occurs in the presence of oxygen, and the following oxidation products are formed: alcohols (ROH), aldehydes (RCHO), ketones (RCOR), carboxylic acids (RCOOH), esters (RCOOR), etc.

A process called reclamation performs the reduction in the amount of acidic contaminants and of other oil oxidation by-products. Typically the oil is percolated through a bed of an adsorbent material. In Brazil, one of the world's leading bauxite producers[4], this mineral is activated at 600°C being the most widely used adsorbent material to perform such a task.

Bauxite is a naturally occurring type of clay with a relatively high surface activity[5]. It is obtained from deposits that supply raw material to aluminum manufacturing plants. Bauxite surface presents aluminum and oxygen atoms, as well as hydroxyl groups (-OH). The selective adsorption of polar molecules depends mainly on hydrogen bonds with Al-OH sites. Therefore, bauxite efficiency in the removal of oxidation compounds is in accord with the following order:

hydroperoxides > acids > alcohols > ketones > hydrocarbons (aromatic and aliphatic)

Insulating oil reclamation provides both technical and economic benefits to electric power utility companies, but the final disposal of used bauxite causes legal and environmental concerns. Around 5% of the mass of oil before reclamation remain adsorbed in the bauxite and turn it into an environmental pollutant. The disposal of bauxite contaminated with insulating oil residues has become very expensive lately due to restrictions imposed by the environmental protection agency of the State of Sao Paulo, Brazil[6-9].

The present study was conducted to develop a method to extract insulating oil residues from activated bauxite by supercritical $CO_2$, thus isolating the contaminants from bauxite and allowing its re-utilization. The method efficiency was tested in a sample of oil that had been previously oxidized in power transformers in service.

## 2. Experimental

### 2.1. Samples

An oil sample was collected from a power transformer in service on the system of the power distribution utility Companhia Paulista de Forca e Luz (CPFL), Brazil. This oil (type AV-58) was manufactured by Petrobras, a Brazilian oil refiner. The percolation of the oil sample was performed through a bed of unused and decontaminated activated bauxite (20-60 mesh) supplied by Mineracao Curimbaba, Brazil.

### 2.2. Gravimetric study of the extraction of spiked samples with Supercritical CO2

This part of the study was planned to evaluate the influence of basic parameters such as supercritical temperature and pressure, flow rate, restrictor system, sample collection system, and others on the extraction of typical compounds frequently found to adsorb in bauxite employed for insulating oils reclamation.

A dynamic extraction system employing a supercritical fluid, developed at the Chromatography Laboratory of the Institute of Chemistry of Sao Carlos (IQSC), University of Sao Paulo, was utilized. A preliminary extraction of the bauxite *in natura* was conducted with $CO_2$ at 200 atm and 60 °C to eliminate contaminants. The process was repeated three times, and a total volume of 750 mL of $CO_2$ was pumped through the sample since the pump flow volume is 250 mL.

The main compounds present in the oil were already identified by high resolution gas chromatography coupled to mass spectrometry (GC-MS) in a previous study[10]. Based on the results obtained, some spiked compounds were selected to represent the most important compound classes present in the oil. Samples of unused and decontaminated bauxite weighing 5.0 g were prepared. Each of them was spiked with 50 mg of one of the following compounds: n-nonadecane, naphthalene, or methyl myristate ester. These compounds were adsorbed by the bauxite samples. The extraction was conducted with supercritical $CO_2$ under the following experimental condition:

- Pressure: 150, 200 and 250 atm;
- Temperature: 50, 60 and 70 °C;
- Restrictor: stainless steel tube with 100 and 250 µm i.d.;
- Extraction duration: 2 min;
- Restrictor length: 50 cm.
- The extracts were collected in test tubes, and the samples were weighed.

### 2.3. Oil residue extraction with Supercritical $CO_2$

A sample weighing 15.0 g of unused and decontaminated bauxite was placed in a glass funnel with a cotton tuft at the bottom. The bauxite was saturated with 300 mL of oxidized insulating oil which was slowly filtered by gravity for 24 hours. The eluted oil was disposed of.

The bauxite sample was divided into three aliquots of 5.0 g each. Three extractions with the dynamic extraction system developed were carried out in accordance with the parameters previously established during the optimization of the experimental conditions for the spiked compounds:

- Temperature: 60 °C;
- Restrictor: stainless steel tube with 250 µm i.d.;
- Extraction time: 2 min;
- Restrictor length: 50 cm.

The extraction pressure was the only parameter changed during this step, being utilized 150, 200 and 250 atm. These three experiments provided three oil extracts, whose chemical composition was further evaluated.

### 2.4. Fractionation by Preparative Liquid Chromatography (PLC-8)

An original oil sample, which was taken as a reference, and the three oil extracts were fractionated by preparative liquid chromatography using the method PLC-8[11]. Each sample weighing 300 mg was placed at the top of a preparative chromatography glass column (50 cm × 11 mm), containing 20 g of silica gel 60 (E.M. Merck, 7734), 70-230 mesh, used as a stationary phase. The silica gel was activated in the oven at 140 °C for 4 hours. The fractions were eluted by an adequate solvent sequence. The elution characteristics and the fractions obtained are presented in Table 1. The increase in solvent polarity produces five hydrocarbon fractions (F-1 through F-5), one intermediate resin fraction (F-6) and two heavy fractions called Asphaltenes (F-7) e asphaltols (F-8).

**Table 1.** Elution condition employed in the Preparative Liquid Chromatography fractionation (PLC-8).

| | Eluent | Elution vol. (mL) | Chemical class |
|---|---|---|---|
| F-1 | Hexane (C-6) | 40 | Saturates |
| F-2 | Hexane (C-6) | 27 | Monocyclic Aromatics |
| F-3 | 11,5% Bz in C-6 | 36 | Dicyclic Aromatics |
| F-4 | 32% Bz in C-6 | 24 | Tricyclic Aromatics |
| F5 | 32% Bz in C-6 | 25 | Polycyclic Aromatics |
| F-6 | Bz: Ac: $MeCl_2$ (3:4:3) | 65 | Resins |
| F-7 | Ac: THF (2:8) | 60 | Asphaltenes |
| F-8 | Methanol | 65 | Asphaltols |

Bz - Benzene $MeCl_2$- Dichloromethane Ac - Acetone THF - Tetra-hydro-furan.

### 2.5. High Resolution Gas Chromatography coupled to Mass Spectrometry (HRGC-MS)

The volatile fractions (F-1 to F-6) of the reference oil and of the three oil extracts were analyzed by HRGC-MS. A Hewlett-Packard gas chromatograph, model 5890 A, fitted with a selective mass detector (MSD), model HP5890, operating in the electron impact mode with 70 eV of ionization energy was used. An in-house fused silica capillary column (50 m × 0.25 mm × 0.7 μm) coated with a film consisting of 5% of phenyl-methylsiloxane / 95% dimethylpolysiloxane was used. The following chromatographic condition were utilized:

- Flow gas : helium (35 cm/s);
- Split ratio: 1:20;
- Injected volume: 1 μL;
- Scan velocity: 1 scan/s;
- Scan interval: 50 – 475 u.m.a.;
- Injector temperature: 250°C;
- Interface temperature: 300°C;
- Oven temperature programming: 80°C (1min) - 4°C/min - 300°C (30min).

F-1 fractions were diluted in 1 mL of hexane for analysis. The other fractions were diluted in 1 mL of dichloromethane. Data process was performed in a CPU, model HP7946. The database used was NBS-REVE.

## 3. Results and discussion

### 3.1. Fractionation of the samples extracted by $CO_2$ employing Preparative Liquid Chromatography (PLC-8)

Table 2 shows the results of the fractionation of the oil samples by the PLC-8 method. The oil extract samples had the relative distribution of most of their fractions changed as compared to that of the reference oil. These results can be at least partly attributed to the fact that bauxite adsorbs the more polar compounds preferentially as compared to hydrocarbons. Saturated hydrocarbons tend to be less retained by bauxite as compared to aromatics since the later fraction contains compounds that are polarizable. The percentages of saturated hydrocarbons (F-1) of the extracted oils were always lower than that of the reference oil. The sum of the relative percentages of the aromatic hydrocarbons (F-2 to F-5) was 16% for the reference oil and 23.4%, 27% and 20.5% for the oil extracts obtained at 150, 200 and 250 atm, respectively. The percentage of resins (F-6) of the oil extracts increased significantly to 7.5% while that of the reference oil was 4.2%. The analyses of the oils by HRGC-MS revealed that there was a high concentration of dicyclic aromatics in fractions F-6 of the oil extracts. Fractions F-7 and F-8 presented a minimum variation.

**Table 2.** Relative distribution (%) of the products obtained from fractionation of the oils by PLC-8.

| Fraction | Reference oil | Oil extract at | | |
|---|---|---|---|---|
| | | 150 atm | 200 atm | 250 atm |
| F-1 | 78.7 | 68.0 | 64.3 | 70.7 |
| F-2 | 12.0 | 18.5 | 21.2 | 13.7 |
| F-3 | 1.6 | 2.0 | 3.3 | 2.8 |
| F-4 | 1.4 | 1.7 | 1.7 | 3.0 |
| F-5 | 1.0 | 1.2 | 0.8 | 1.0 |
| F-6 | 4.2 | 7.5 | 7.5 | 7.5 |
| F-7 | 0.6 | 0.7 | 0.7 | 0.8 |
| F-8 | 0.5 | 0.4 | 0.5 | 0.5 |

### 3.2. Gravimetric study of Supercritical $CO_2$ extraction of spiked samples

The results from the extraction of spiked samples are presented in Tables 3 to 5. As the data show, the best extraction results for the three spiked samples studied were obtained at 200 atm of pressure, and at temperatures of 60 and 70°C, with the restrictor with 250 µm of internal diameter. Under such a condition, extraction was 97% in mass for methyl myristate, and 98% for both naphthalene and n-nonadecane.

The extraction at 150 atm (Table 3) had the worst performance since the percentage of spiked extractions reached a maximum of 50% in mass. The extraction at 250 atm (Table 5) presented better results than those obtained at the extraction at 150 atm, and reached up to 85% in mass. However, these results were poorer than those of the extraction at 200 atm (Table 4).

**Table 3.** Influence of the temperature and restrictor diameter on the extraction of spiked oil employing $CO_2$ at 150 atm as the extraction solvent.

| Temperature (°C) | Restrictor diameter (µm) | Extraction percentage (%) | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| 50 | 100 | 12 | - | 25 |
| 60 | 100 | 12 | - | 28 |
| 70 | 100 | 12 | - | 25 |
| 50 | 250 | 35 | 10 | 35 |
| 60 | 250 | 48 | 10 | 50 |
| 70 | 250 | 48 | 10 | 50 |

1- n-nonadecane; 2 - naphtalene; 3 – methyl myristate.

**Table 4.** Influence of the temperature and restrictor diameter on the extraction of spiked oil employing $CO_2$ at 200 atm as the extraction solvent.

| Temperature (°C) | Restrictor diameter (µm) | Extraction percentage (%) | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| 50 | 100 | 75 | 80 | 75 |
| 60 | 100 | 88 | 90 | 91 |
| 70 | 100 | 86 | 93 | 93 |
| 50 | 250 | 97 | 96 | - |
| 60 | 250 | 98 | 98 | 97 |
| 70 | 250 | 98 | 98 | 97 |

1- n-nonadecane; 2 - naphtalene; 3 - methyl myristate.

**Table 5.** Influence of the temperature and restrictor diameter on the extraction of spiked oil employing $CO_2$ at 250 atm as the extraction solvent.

| Temperature (°C) | Restrictor diameter (µm) | Extraction percentage (%) | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| 50 | 100 | 70 | 70 | 70 |
| 60 | 100 | 85 | 85 | 88 |
| 70 | 100 | 85 | 85 | 85 |
| 50 | 250 | 75 | 78 | 75 |
| 60 | 250 | 76 | 75 | 75 |
| 70 | 250 | 77 | 78 | 75 |

1- n-nonadecane; 2 - naphtalene; 3 - methyl myris.

### 3.3. High Resolution Gas Chromatography coupled with Mass Spectrometry (HRGC-MS) profile of oil samples extracted by Supercritical $CO_2$

It was possible to visually confirm that the extraction process of real oil samples presented satisfactory results. Figure 1 shows test tubes containing samples of new bauxite before use, bauxite with oil residues before and after extraction, as well as a glass container with oil residue extracted at 200 atm. The visual aspect of the bauxite after extraction is very close to that of the new one which was used as a blank.

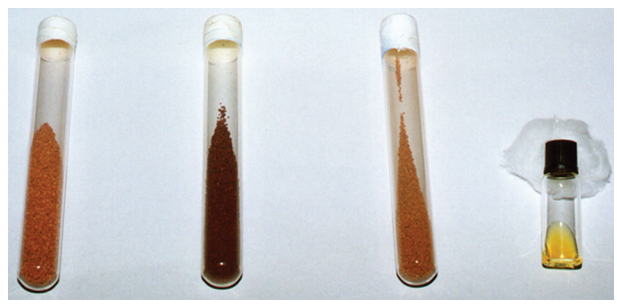

**Figure 1.** Test tubes containing: (a) samples of new bauxite before use; (b) contaminated bauxite containing oil residues before extraction; (c) bauxite after extraction; (d) a glass container with oil residue extracted at 200 atm.

Figure 2 show the chromatograms of fraction F-1 of the clean oil used as a reference and of the oil samples obtained from the same oil after extraction with supercritical $CO_2$ at 150, 200, and 250 atm of pressure, respectively.

The compounds whose peaks are shown in Figure 2 after 50 minutes of elution time correspond to a homologous series of long-chain carboxylic acids. The carboxylic acids were expected to elute mostly at resin fraction (F-6). However, they were detected in all of the previous fractions from F-1 through F-5 of the reference oil (figures 4a, 5a, and 6a). Because of the high molecular weight of such acids, which is evidenced by their long retention time, we noticed a poor elution selectivity of the more polar solvents used in the fractionation by the PLC-8 method. The long hydrocarbon chain bonded to the acid radicals also has a good affinity for the less polar solvents and for hexane. Figure 3 shows the fragmentogram of a typical long-chain carboxylic acid detected in fraction F-1 of the reference oil.

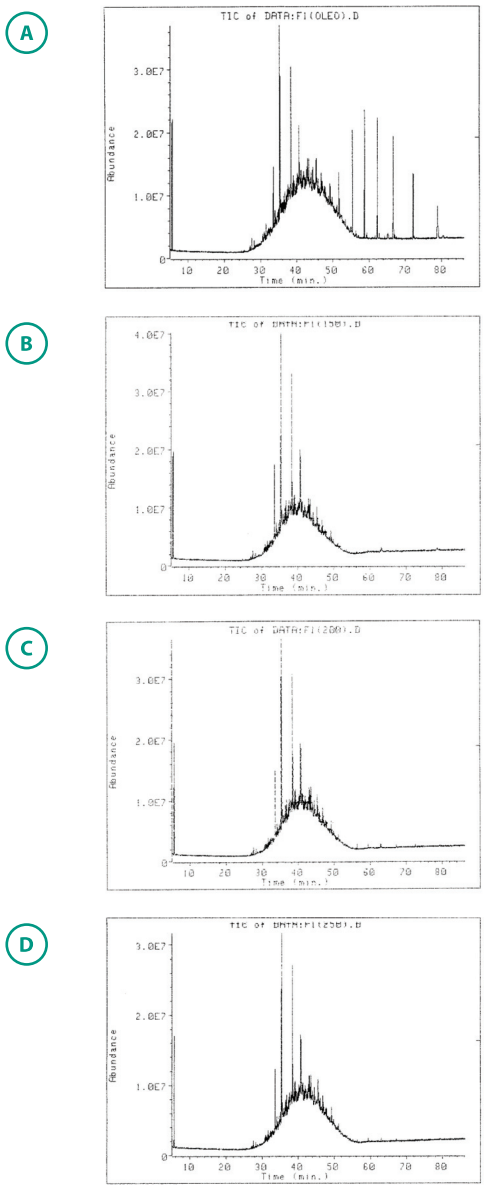


**Figure 2.** TIC of fractions F-1. (a) reference oil; (b) oil extract obtained by DYN-SFE at 150 atm; (c) oil extract obtained by DYN-SFE at 200 atm; (d) oil extract obtained by DYN-SFE at 250 atm.

A satisfactory extraction of linear and branched long-chain alkanes detected up to a retention time of approximately 50 minutes was obtained. The carboxylic acids that eluted thereafter were extracted at very low concentration and only at the pressure of 200 atm.

The monocyclic aromatic hydrocarbon fractions (F-2) of the four samples analyzed presented few compounds detected within a retention time up to 50 minutes (Figure 4). However, a significant concentration of carboxylic acids was detected thereafter in the reference oil sample (Figure 4a). The compounds eluting at a retention time before 50 minutes were successfully extracted at the three pressures used. A significant extraction of the carboxylic acids was obtained only in the extraction performed at 200 atm. No detectable extraction of these acids was observed at the other extractions.

The di-, tri- and polycyclic aromatic hydrocarbon fractions (F-3 and F-4) analyzed also presented very few compounds detected within a retention time up to 50 minutes. Figure 5 show the chromatograms of fractions F-3, F-4 and F-5 of the reference oil, respectively. The chromatograms obtained from the extractions of all of these three fractions were extremely poor for the oil extracts obtained at 150, 200, and 250 atm. No significant extraction of any class of compounds was observed in such cases.

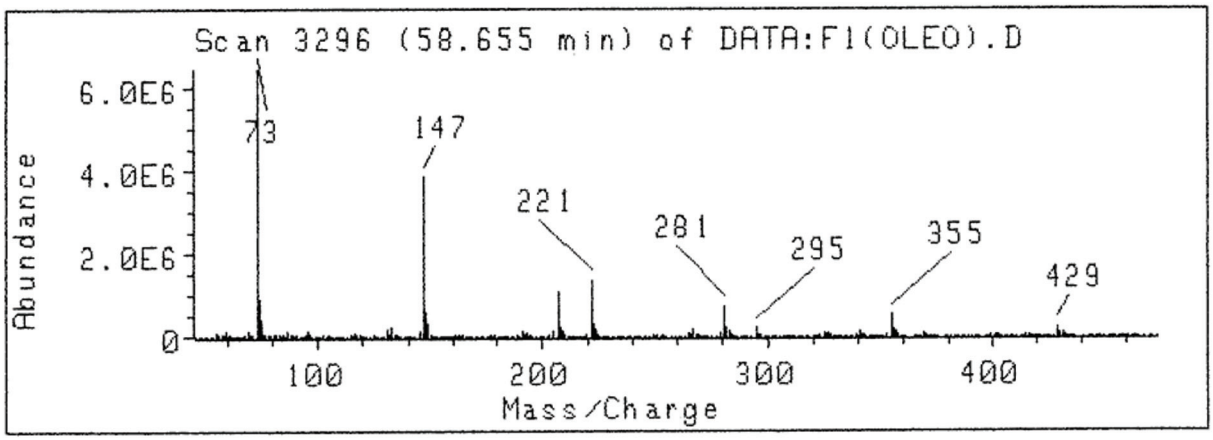


**Figure 3.** Fragmentogram of a long-chain carboxylic acid (retention time at 58,655 min), detected in the saturated hydrocarbon fraction of the reference oil.

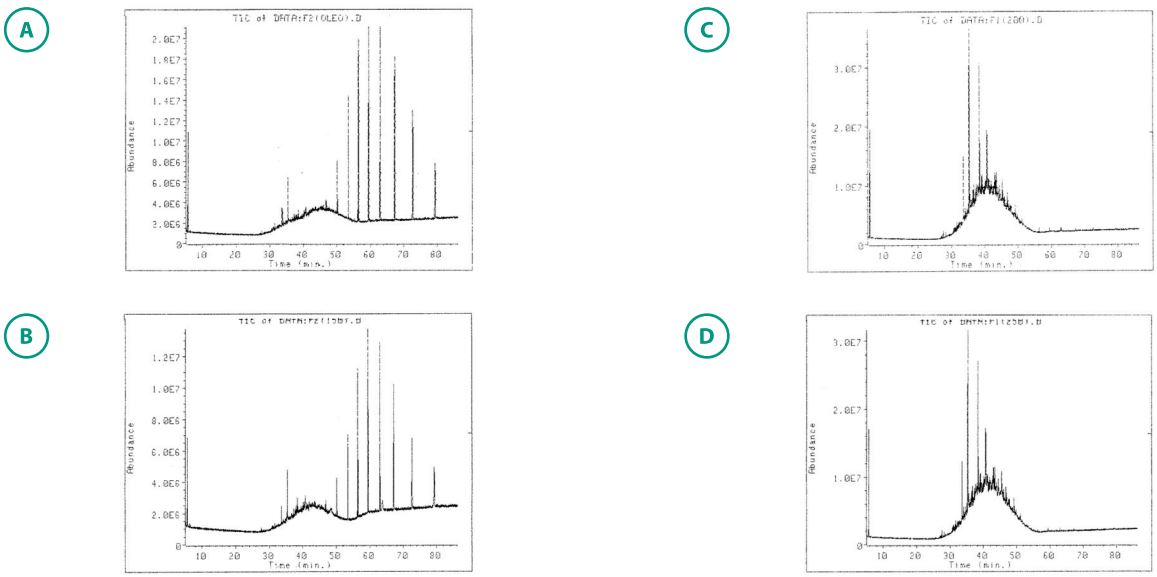


**Figure 4.** TIC of fractions F-2. (a) reference oil; (b) oil extract obtained by DYN-SFE at 150 atm; (c) oil extract obtained by DYN-SFE at 200 atm; (d) oil extract obtained by DYN-SFE at 250 atm.

The resin fraction (F-6) of the reference oil presented a low concentration of compounds up to a retention time of approximately 46 minutes (Figure 6a). However, thereafter a significant concentration of carboxylic acids was comparatively detected once again.

Several compounds were extracted in the experiments conducted with the contaminated bauxite at the three pressures employed. Taking into consideration the data of the extraction performed at 250 atm (Fig. 6d), it is possible to conclude that the more intense peaks refer to long linear chain alkanes with retention times varying from 33 – 39 minutes; athracenone isomers, with retention times of 39.623, 40.630 and 41.018 minutes; and aromatic compounds bonded to alkyl groups with a retention time range from 41 – 48 minutes. The majority of the compounds with retention times before 50 minutes were successfully extracted in the three extractions performed. However, the extraction of the carboxylic acids has to be further investigated in order to better understand its behavior.

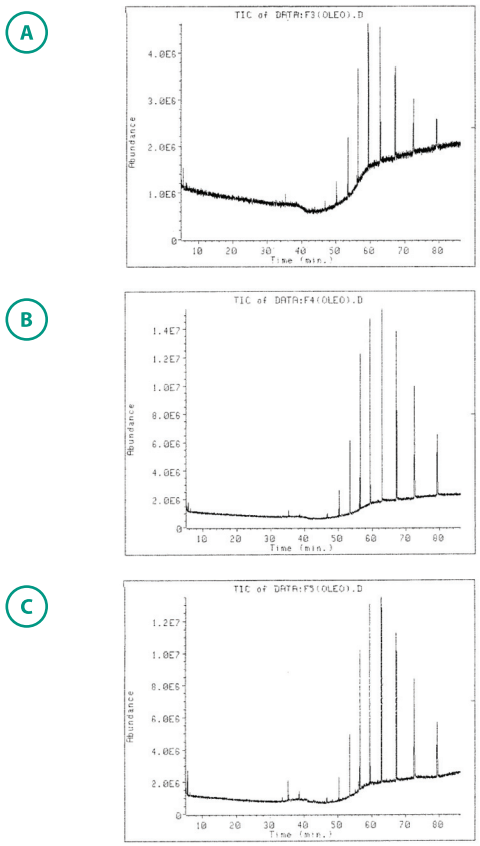


**Figure 5.** TIC of fractions from the reference oil; (a) F-3; (b) F-4; (c) F-5.

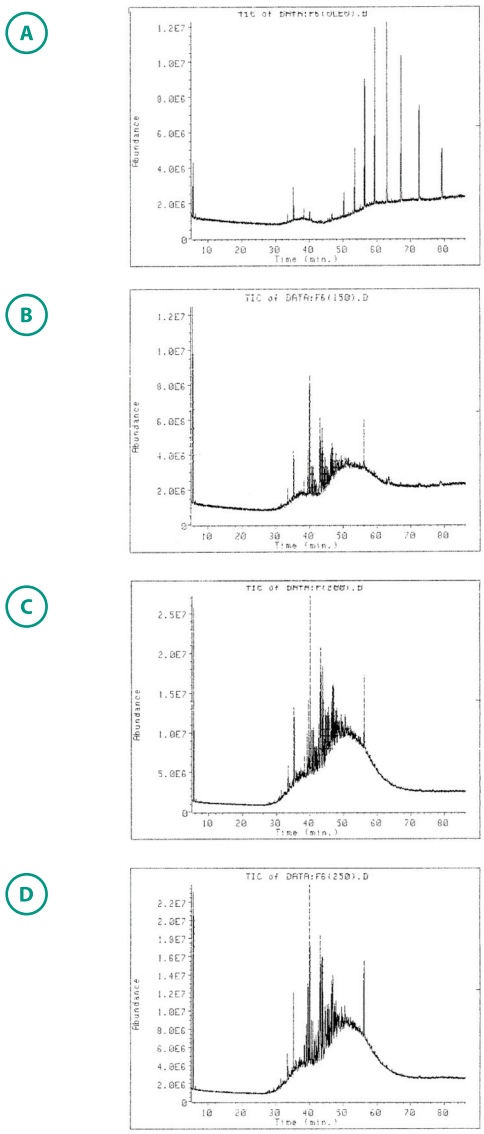


**Figure 6.** TIC of fractions F-6. (a) reference oil; (b) oil extract obtained by DYN-SFE at 150 atm; (c) oil extract obtained by DYN-SFE at 200 atm; (d) oil extract obtained by DYN-SFE at 250 atm.

## 4. Conclusion

The main components of the several classes of chemical compounds of an electrical-grade insulating oil sample were determined by preparative liquid chromatography fractionation employing the method PLC-8 and by high resolution gas chromatography coupled with mass spectrometry (HRGC-MS).

The method developed to extract by supercritical carbon dioxide the residues of insulating oil adsorbed in activated bauxite was effective to extract spiked compounds in a preliminary study. The described method was also effective in extracting the majority of the compounds detected in the insulating oil studied. However, the extraction of carboxylic acids from oil oxidation requires to be optimized in a future study. Modifiers such as methanol and ethanol, among others are being investigated aiming to improve the extraction efficiency of this particular class of contaminants.

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# The US Presidents' Example: An Anthropomorphic Explanation of Comprehensive Two-Dimensional Gas Chromatography with Mass Spectrometric Detection (GCxGC/MS)

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**Abstract**

In this paper we have developed an analogy to gas chromatography and mass spectrometry in order to explain the key concepts in the use of comprehensive two-dimensional chromatography with mass spectrometry detection (GCxGC/MS). The analogy makes use of the "separation" technique called namography and the "identification" technique called alphabetography to separate individual components from complex mixtures of human names. An example involving the use of the 44 US presidents is used. Software was also developed to provide an interactive platform where students and other interested users can create their own signals to and test their own complex name samples.

**Keywords:** Namography, Alphabetography, GCxGC/MS.

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## 1. Introduction

Professor Harold M. McNair has been at the forefront of the development of gas chromatography (GC) since its humble beginnings as a novel analytical instrument in the late 1950s, and has been an enthusiastic mentor to generations of practitioners around the world for the past 6 decades through countless workshop lectures that he has organized at conferences such as PittCon, ACS, and COLACRO. His many technical contributions have been reported in the peer-reviewed literature, and his overviews of the state-of-the-art in GC instrumentation and application development have recently been updated in his book entitled "Basic Gas Chromatography"[1]. As a conscientious educator, Prof. McNair has always put a lot of effort to incorporate the latest audio/visual technology to allow his course participants to access his lecture material after attending the workshop in person, and this technology has evolved over the years from the use of VCR tapes in the 1970s and 1980s to the use of electronic material that can be accessed or downloaded from websites since the advent of the internet in the early 1990s[2,3].

In this contribution to Prof. McNair's 80th birthday, we report the development of educational materials that we have designed to accompany our introductory workshops on the emerging technology of comprehensive two-dimensional gas chromatography (GCxGC). GCxGC is an exciting high-resolution separation science technology that was patented in the laboratory of the late Prof. John B. Phillips in 1991[4], and whose scope has gradually increased in the past decade with the first generation of commercially available instruments. Advances in GCxGC instrumentation and applications have appeared in nearly 1000 peer-reviewed journal articles, and a few books have been published that present some exciting analyses for a variety of application areas that range from industrial QA/QC methods (petroleum, food and fragrance, metabolomics) to government regulatory protocols (environmental monitoring, biomonitoring)[4-13]. A clear understanding of GCxGC concepts is needed by a growing number of scientists inside and outside of the field. It is within this context that we have worked on an analogy (with accompanying software) that surveys some key concepts of GCxGC within the scope of GC-based instruments. Mass spectrometry (MS) detection is also highlighted as a suitable technology to interface with GCxGC for the enhanced analysis of complex mixtures.

Analogical reasoning is ubiquitous to human cognition, and the use of analogies in teaching is a well established pedagogical tool[14]. The goal of analogical teaching is to establish bridges between concepts in a familiar domain (analog or source concepts) and the concepts in an unfamiliar domain (target concepts). The basic intuition behind analogical reasoning is that when there are substantial parallels between the analog and target concepts, there are likely to be further parallels. Well known scientific analogies include the electricity/water flow example in physics, the molecular motion/billiards ball collision example in chemistry, the heart/car engine example in medicine, where the analog concepts serve as mental models to support the reasoning/connectivity of the concepts in the target domain. Research-based models for scientific analogies have been developed[14] that involve the following guidelines to foster understanding and minimize misconceptions: 1) Introduction of the target concept, 2) Review of the analog concept, 3) Identification of the relevant features between the analog and the target concepts, 4) Mapping of the similarities between analog and target concepts, 5) Identification of the limits beyond which the analogy breaks down, and 6) Conclusions and feedback.

The premise for the anthropomorphic analogy of GCxGC/MS that was chosen for this work is illustrated in Figure 1. Anthropomorphic analogies involve the transfer of human attributes to non-human phenomena. The use of anthropomorphism in scientific teaching strategies offers the advantage that analog concepts are typically well understood, making it easier to establish connections to the target concepts of interest[15]. Chemical compounds are similar to

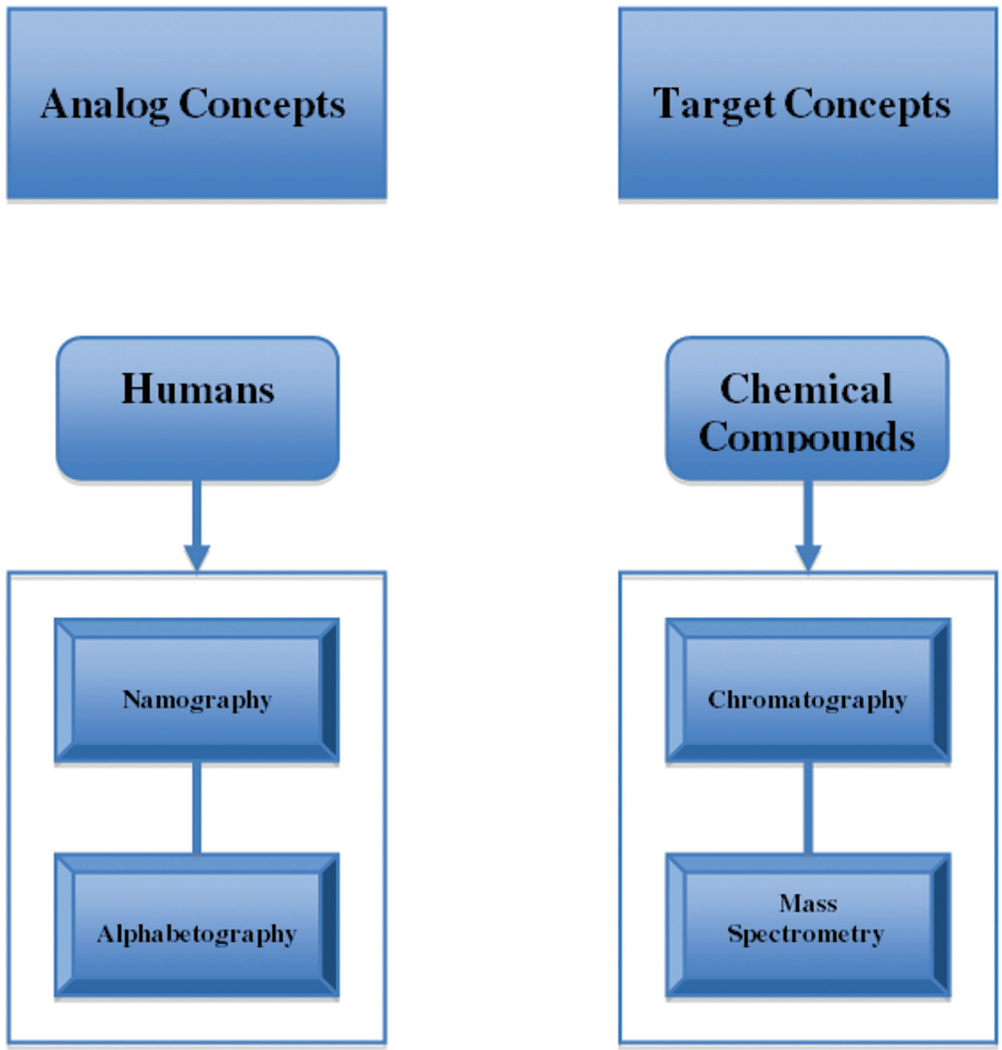



**Figure 1.** Conceptual representation of the GC-MS/ namography-alphabetography analogy.

human beings in the sense that they possess a unique set of defining characteristics (properties) such as their names, identification numbers, heights, shapes, etc. We define two analytical techniques: namography, which is analogous to GC, and alphabetography, which is analogous to MS. In namography, a mixture of names is sent through a "name separator" that filters the names through the system on the basis of the number of letters in the name. In alphabetography, a mixture of letters in a name are sent through a "letter sorter" that generates an alphabet histogram. Namograms are signals that intend to produce one peak per compound, whereas alphabetograms produce a series of peaks in the alphabet "spectrum" that are related to a given name (compound). The relative intensities of the ensemble of peaks in the alphabetogram can be used as a fingerprint that can be used for the unique identification of the name. Even though the process of differential migration (solute/stationary phase interaction) is not explicitly defined in namography, the result of the separation process is analogized. Likewise, in alphabetography the ionization process and the generation of molecular ions and fragments are not explained, but the idea of a single compound being broken down into a set of signals that provide information on the structural relationships in that compound are retained in the analogy.

The goal of the namography/alphabetography combination is thus the full separation and identification of all the names in a given name mixture. In this paper we focus on the US presidents as a model sample to present several key concepts such as the impact of stationary phase on the elution order and the co-elution problem in GC, mass spectral deconvolution and mass spectral similarity matching in MS, as well as ordered structuring and resolution enhancement in GCxGC.

## 2. Experimental

### 2.1. Samples

A list 50 names (and their respective heights in centimeters) was obtained from a number of internet sites and reference books[16-18]. The names include the 44 US presidents, which are shown in Table 1. In addition, the names and heights of the presidential contenders in each of the last four elections were also obtained from the same website. These additional names are: Albert Gore from the 2000 election (185 cm), John Kerry from the 2004 election (193 cm), John McCain from the 2008 election (175 cm), and Willard Romney from the 2012 election (188 cm). A couple of vice-presidential candidates from the 2000 election were also included in the project: Richard Cheney (173 cm) and Joseph Lieberman (175 cm).

### 2.2. Sample Analysis

Conceptual diagrams of the namography and alphabetography techniques are shown in Figure 2. In the namography diagram (Figure 2A), the analyzer is represented as a capillary column that sorts the components of a mixture of different peoples's names on the basis of the length of the name. The resulting signal is a plot of name length (x-axis) versus person's height (y-axis). It is implied that the length of the name is related to the time it takes for the compound to go through the system (its retention time). The detector is called a feature identification device (FID) that functions as a single-channel sensor is a manner similar to flame ionization detectors in GC.

In the alphabetography diagram (Figure 2B), the analyzer is represented as a letter sorter. The letters in a person's name are broken up into their individual letters, and sorted according to their position in the alphabet. The resulting signal is a profile of the person's name in the alphabet (x-axis) in terms of the relative abundance of the letters (y-axis) present in the name. The alphabetogram is a multi-channel detection device, in contrast to the single-channel FID that does not sort the letters but only detects the number of letter that pass through it at a given time determined by the name length.

The two-dimensional namography instrument with alphabetography detection is illustrated in Figure 2C. The two dimensional namogram assembles two separation mechanisms, and names are separated on the basis of their last name in the primary column, and then separated on the basis of their first name in the secondary column. The detection signal produced by this arrangement is a three-dimensional surface plot in which the last name length is displayed in the x-axis, the first name length is displayed in the y-axis, and the person's height is displayed in the z-axis. The plot can also be viewed in the contour format, where the signal information from the surface plot is projected onto a 2D plane (as shown in Figure 2C) and the peak height is recorded by the color intensity. The alphabetography information is typically not visually displayed because plots that involve more than three dimensions are not as easily displayable. However, the alphabet profile information is available for further analysis.

### 2.3. Data Processing Software

The basic flow chart of the software that was developed for this project is shown in Figure 3A. The required input data for the program is the first and last name and the height. The data is then processed according to the following parameters: 1) name length of the first name, 2) name length of the last name, 3) a string concatenation of the first and last name, 4) the generation of the alphabet histogram on the basis of the concatenated name string, 5) the normalization of the

**Table 1.** List of Names Used in this Project.

| | Last Name | First Name | | Height (cm) |
|---|---|---|---|---|
| 1 | Washington | George | President, 1789-1797 | 187 |
| 2 | Adams | John | President, 1791-1801 | 170 |
| 3 | Jefferson | Thomas | President, 1801-1809 | 189 |
| 4 | Madison | James | President, 1809-1817 | 163 |
| 5 | Monroe | James | President, 1817-1825 | 183 |
| 6 | Adams | John | President, 1825-1829 | 171 |
| 7 | Jackson | Andrew | President, 1829-1837 | 185 |
| 8 | Van Buren | Martin | President, 1837-1841 | 168 |
| 9 | Harrison | William | President, 1841 | 173 |
| 10 | Tyler | John | President, 1841-1845 | 170 |
| 11 | Polk | James | President, 1845-1849 | 173 |
| 12 | Taylor | Zachary | President, 1849-1850 | 173 |
| 13 | Fillmore | Millard | President, 1850-1853 | 175 |
| 14 | Pierce | Franklin | President, 1853-1857 | 178 |
| 15 | Buchanan | James | President, 1857-1861 | 183 |
| 16 | Lincoln | Abraham | President, 1861-1865 | 194 |
| 17 | Johnson | Andrew | President, 1865-1869 | 178 |
| 18 | Grant | Ulysses | President, 1869-1877 | 173 |
| 19 | Hayes | Rutherford | President, 1877-1881 | 174 |
| 20 | Garfield | James | President, 1881 | 183 |
| 21 | Arthur | Chester | President, 1881-1885 | 183 |
| 22 | Cleveland | Grover | President, 1885-1889 | 180 |
| 23 | Harrison | Benjamin | President, 1889-1893 | 168 |
| 24 | Cleveland | Grover | President, 1893-1897 | 180 |
| 25 | McKinley | William | President, 1897-1901 | 170 |
| 26 | Roosevelt | Theodore | President, 1901-1909 | 178 |
| 27 | Taft | William | President, 1909-1913 | 183 |
| 28 | Wilson | Woodrow | President, 1913-1921 | 180 |
| 29 | Harding | Warren | President, 1921-1923 | 183 |
| 30 | Coolidge | Calvin | President, 1923-1929 | 178 |
| 31 | Hoover | Herbert | President, 1929-1933 | 182 |
| 32 | Roosevelt | Franklin | President, 1933-1945 | 188 |
| 33 | Truman | Harry | President, 1945-1953 | 175 |
| 34 | Eisenhower | Dwight | President, 1953-1961 | 179 |
| 35 | Kennedy | John | President, 1961-1963 | 183 |
| 36 | Johnson | Lyndon | President, 1963-1969 | 193 |
| 37 | Nixon | Richard | President, 1969-1974 | 182 |
| 38 | Ford | Gerald | President, 1974-1977 | 183 |
| 39 | Carter | James | President, 1977-1981 | 177 |
| 40 | Reagan | Ronald | President, 1981-1989 | 185 |
| 41 | Bush | George | President, 1989-1993 | 188 |
| 42 | Clinton | William | President, 1993-2001 | 188 |
| 43 | Bush | George | President, 2001-2009 | 182 |
| 44 | Obama | Barack | President, 2009- to date | 185 |
| 45 | Romney | Willard | 2012 Presidential Candidate | 188 |
| 46 | McCain | John | 2008 Presidential Candidate | 175 |
| 47 | Kerry | John | 2004 Presidential Candidate | 193 |
| 48 | Gore | Albert | 2000 Presidential Candidate | 185 |
| 49 | Cheney | Richard | 2000 Vice-Presidential Candidate | 173 |
| 50 | Lieberman | Joseph | 2000 Vice-Presidential Candidate | 175 |

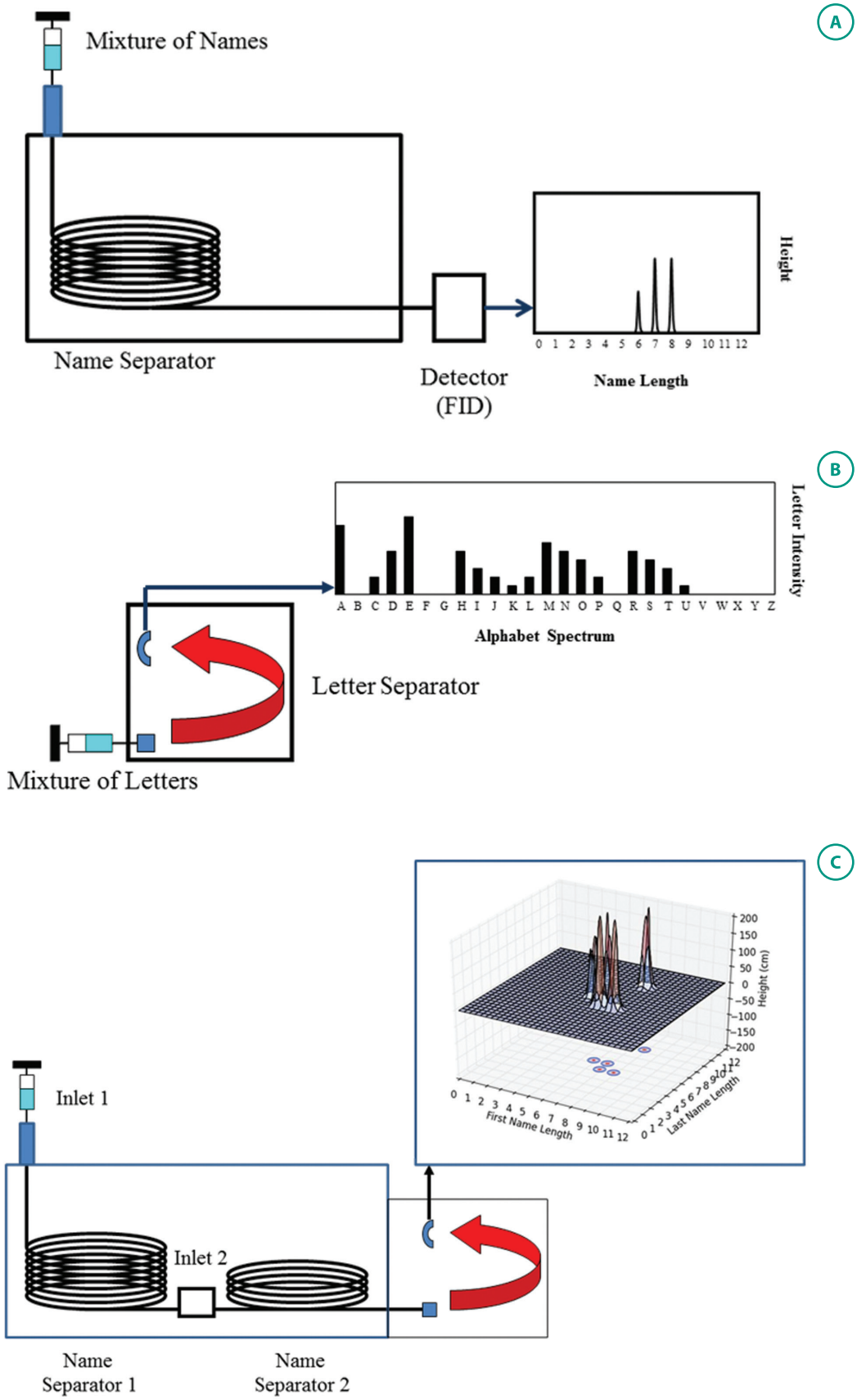
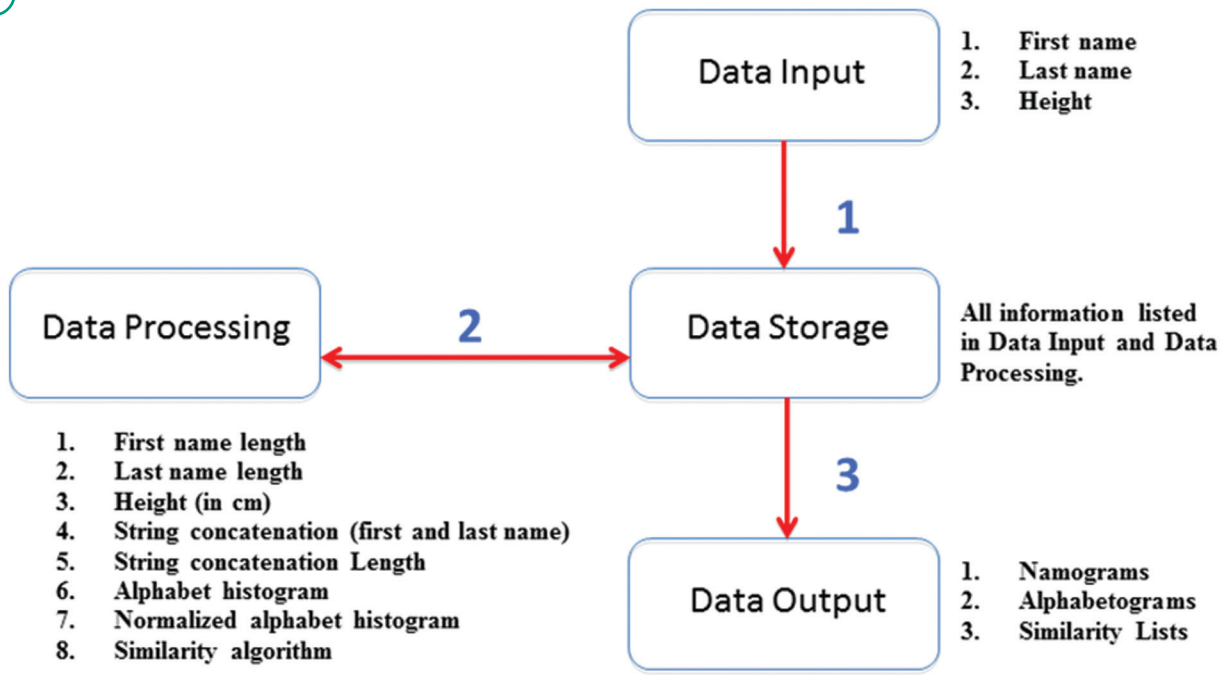



**Figure 2.** A. Namography system. B. Alphabetography system. C. 2D-Namography/Alphabetography system.

A

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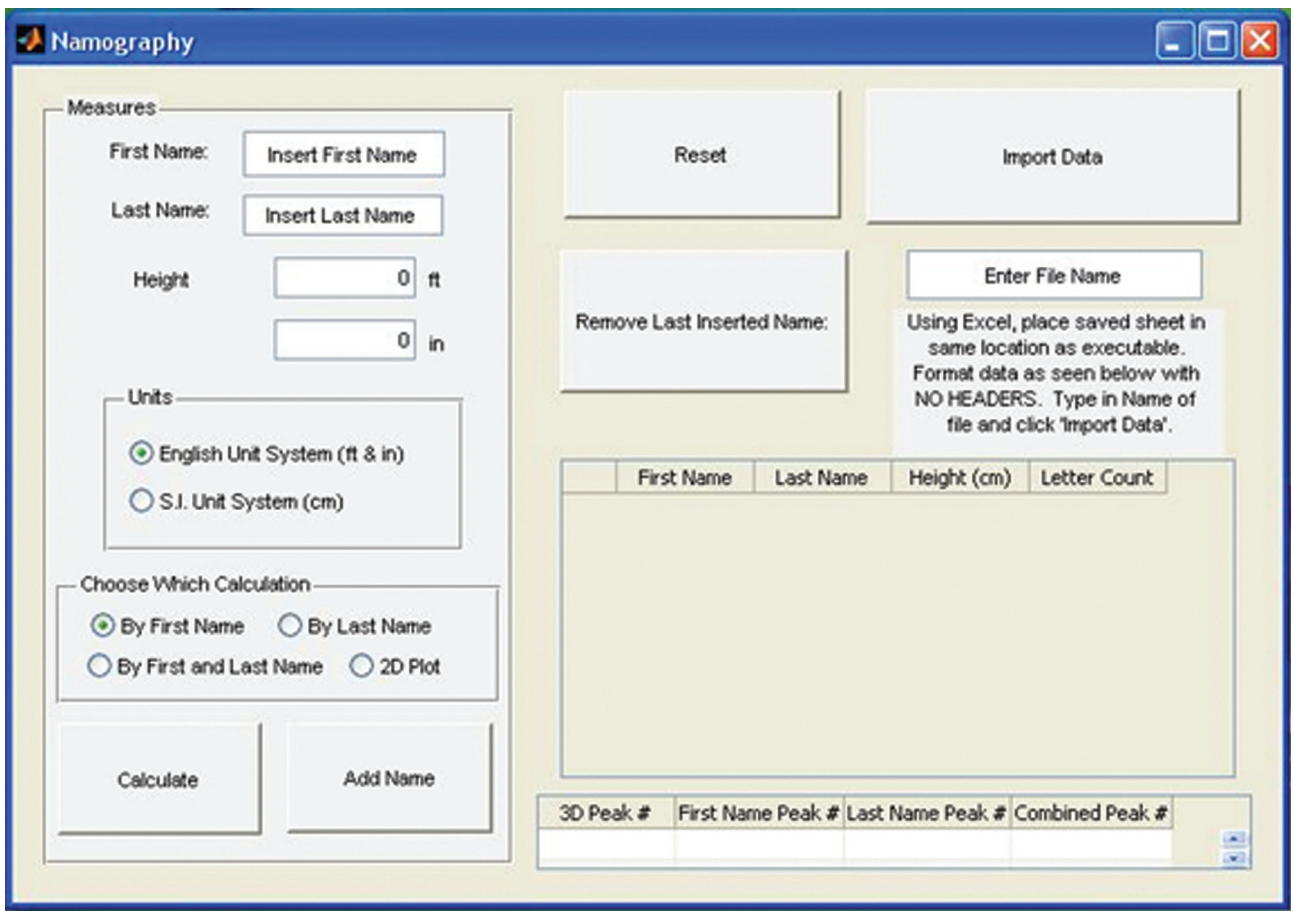



**Figure 3.** A. Overview of software program design. B. Matlab GUI of the program.

alphabet histogram on the basis of the tallest peak in the profile. All processed data is stored in a database, where the information is available to be further processed for the output selection of the user's choice. Data outputs include namogram signals (for a single name, a group of names, or two-dimensional plots), and alphabetogram signals (for a single name or a group of names). For alphabetogram profiles, a library searching algorithm was also developed that computes the Euclidian distance measurement of a given alphabet profile (or group of alphabetograms) to each entry in the database, and returns a similarity hit list that is analogous to library search reports produced in mass spectrometry. A deconvolution algorithm was also included for the separation of alphabetogram signals that are the product of co-eluting namogram peaks.

All basic functionalities were initially developed and tested in Excel (version 12, Microsoft, Redmond, USA). These functionalities were then subsequently transferred to programs in Matlab 8 (Mathworks, Natick, USA) and Python 2.7.1 (Python Software Foundation, Delaware, USA). Graphic user interfaces (GUIs) were developed in both platforms (the GUI for Matlab is shown in Figure 3B) for easy user interaction. The Matlab version was designed to produce an executable file to be available for installation and use on individual PC machines, whereas the Python program was developed to be used on an internet website.

## 3. Results and Discussion

The approach to explain the connections between the analog concepts of namography/alphabetography and the target concepts of GC/MS involved three target scenarios:

4. The analysis of a single person's name: President George Washington (the first US president).
5. The analysis of a simple mixture of 2 names: the presidential candidates in the most recent US elections (since the year 2000).
6. The analysis of a complex mixture: the 44 US presidents.

### 6.1. Single Compound Analysis

An application of the namography and alphabetography techniques is demonstrated for a single person in Figure 4. A single person, representing a single compound, can be analyzed on several different namogram systems (or stationary phases) according to which "property" is selected for the analysis. In Figure 4A and 4B, President George Washington is analyzed on the basis of his first and last names, respectively, and the single peaks at position 6 (in Figure 4A) and position 10 (in Figure 4B) represent the specific interaction of those "properties" of his name with the "stationary phase" of the system. Even though all of the person's properties are present, the stationary phase selectively interacts with the property of choice, which is a useful feature in chromatographic analysis.

Figure 4C shows the "raw" alphabetogram of President Washington. The alphabetogram is the result of the sorting of all letters in both the first and last names because (like mass spectra) the signal profile it generates is consistent regardless of which namogram system is being used. Even though the original name cannot be reconstituted just from looking at the peak profile, the relative abundances of these letters in the name form a unique fingerprint that is different from others. Storage of this fingerprint in a database will allow for its identification in an unknown sample via the use of a mathematical algorithm that computes the relative distance of the spectral profile in the unknown to the spectral profile of the stored standard. In this manner, the spectrum that most resembles the unknown spectrum is identified, and the algorithm returns a degree of certainty of this match that is called a similarity value.

Figure 4D shows the normalized alphabetogram of the profile shown in Figure 4C, in which the peak with the largest abundance of letters in the profile is given a nominal value of 100, and the abundance of all the other peaks in the peak profile are recalculated according to their relative abundance to the peak maximum. Profile normalization is an important procedure that helps in generating consistent profiles when the concentration

of the compound changes. Even though normalization is not necessary in this particular analogy (because the alphabetograms are already normalized, since the concentrations of the names don't change), it is included because it is an important step in the data processing protocol, and helps in the understanding of the spectral deconvolution and spectral matching algorithms.

Since the alphabetograms are consistent for a compound, names can be identified when compared to a database of stored alphabetograms. In Figure 5A the results of a library search are shown for President Washington. Library hit lists are generated by comparing a name profile to all other profiles in the database. These profile differences are then ranked and given a similarity value on a scale of 1000. In Figure 5A, the search for President Washington returns a perfect match since the name of the unknown is already in the library. However, library searches can be done for names outside of the library as well. In these instances, the library will return a list of hits that most closely resemble the unknown profile. This case is demonstrated in Figures 5B and 5C, where the alphabetogram of Prof. McNair is compared to the President's database to find out which president's name most closely resembles the name of our distinguished friend. Figure 5B shows a juxtaposition of normalized alphabet profiles between Prof. McNair and president Washington that gives a visual outline of the similarities and differences between the two names, and returns a similarity matching value (744). The ranking of the top names to Prof. McNair is given in Figure 5C. Prof. McNair will probably be pleased that the top name on his similarity search list is that of President Abraham Lincoln, one of the most revered US presidents!

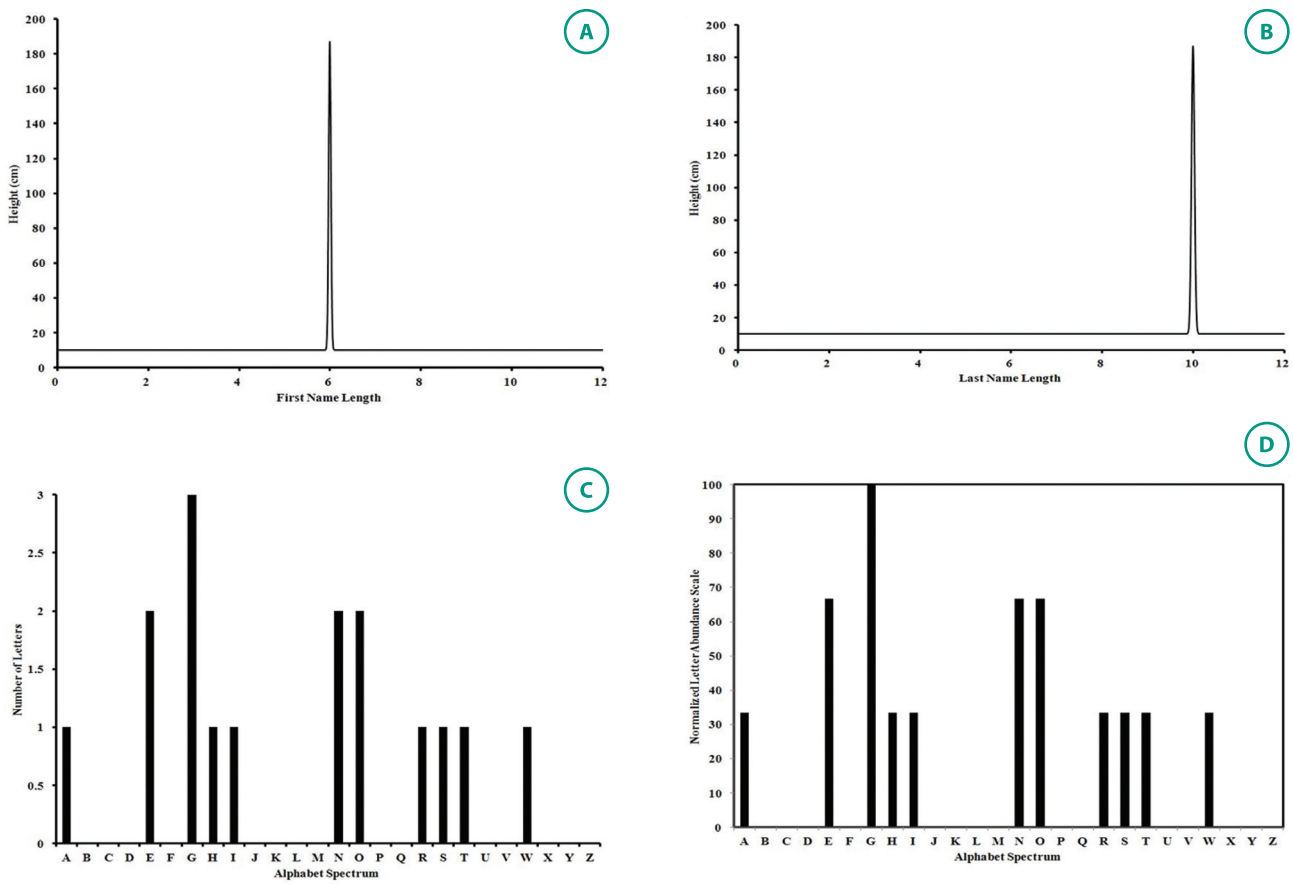



**Figure 4.** Single person analysis. A. Namogram for President Washington (Last Name stationary phase). B. Namogram for President Washington (First Name stationary phase). C. Raw Alphabetogram for President Washington. D. Normalized Alphabetogram for President Washington.

### 6.2. Simple Mixture Analysis

In the next set of results, a presentation of analyses for two-compound mixtures are presented, and in Figure 6 the namograms of the past four presidential elections are shown. In our workshops, we postulate the hypothesis that namography is capable of predicting the winner of US presidential elections through the use of a last name stationary phase analysis, with the winner being the faster eluter of the two presidential candidates. Our predictions show successful results in the 2012 (Obama over Romney), 2008 (Obama over McCain) and 2004 (Bush over Kerry) elections, as shown in

A

| Value | Name | Similarity |
|---|---|---|
| 1 | Washington, George | 1000 |
| 2 | Johnson, Andrew | 885 |
| 3 | Eisenhower, Dwight | 872 |
| 4 | Harding, Warren | 859 |
| 5 | Bush, George | 846 |
| 6 | Bush, George | 846 |
| 7 | Wilson, Woodrow | 824 |
| 8 | Roosevelt, Theodore | 824 |
| 9 | Reagan, Ronald | 821 |
| 10 | Harrison, Benjamin | 821 |

B

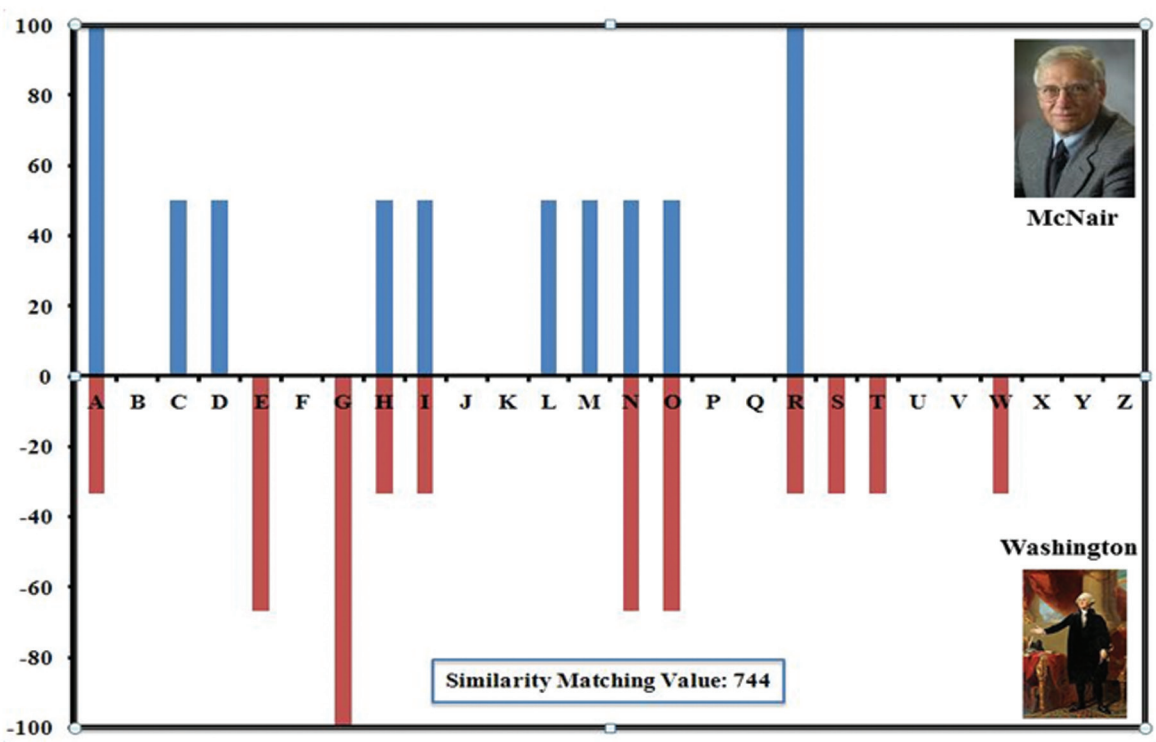



**Figure 5.** Alphabetogram Library Searching. A. Library hit results for a name in the library database. B. Alphabetogram Profile Comparison an unknown and a library standard. C. Library hit results for a name outside of the library database.

Figures 6A-C. The results for the 2000 election are more problematic (Figure 6D) due to the fact that the two names (Bush and Gore)cannot be separated due to the fact that the have the same name length. The 2000 election is an example of a co-elution problem, and the difficulty of this separation explains the challenge in the resolution of this particular election. One of the solutions to the separation of co-eluting compound pairs in GC is to change the stationary phase in order to change the selectivity mechanism. However, in the case of these two candidates, a change to a first name stationary phase results in another co-elution since George (Bush) and Albert (Gore) both contain 6 letters. Even their middle names (Walker and Arnold) are not separable by name length. Since the presidential candidates co-elute in all the possible namogram systems, our solution to the election expanded to the vice-presidential candidates, as shown in Figure 6D. Since Cheney (Bush's running mate) was

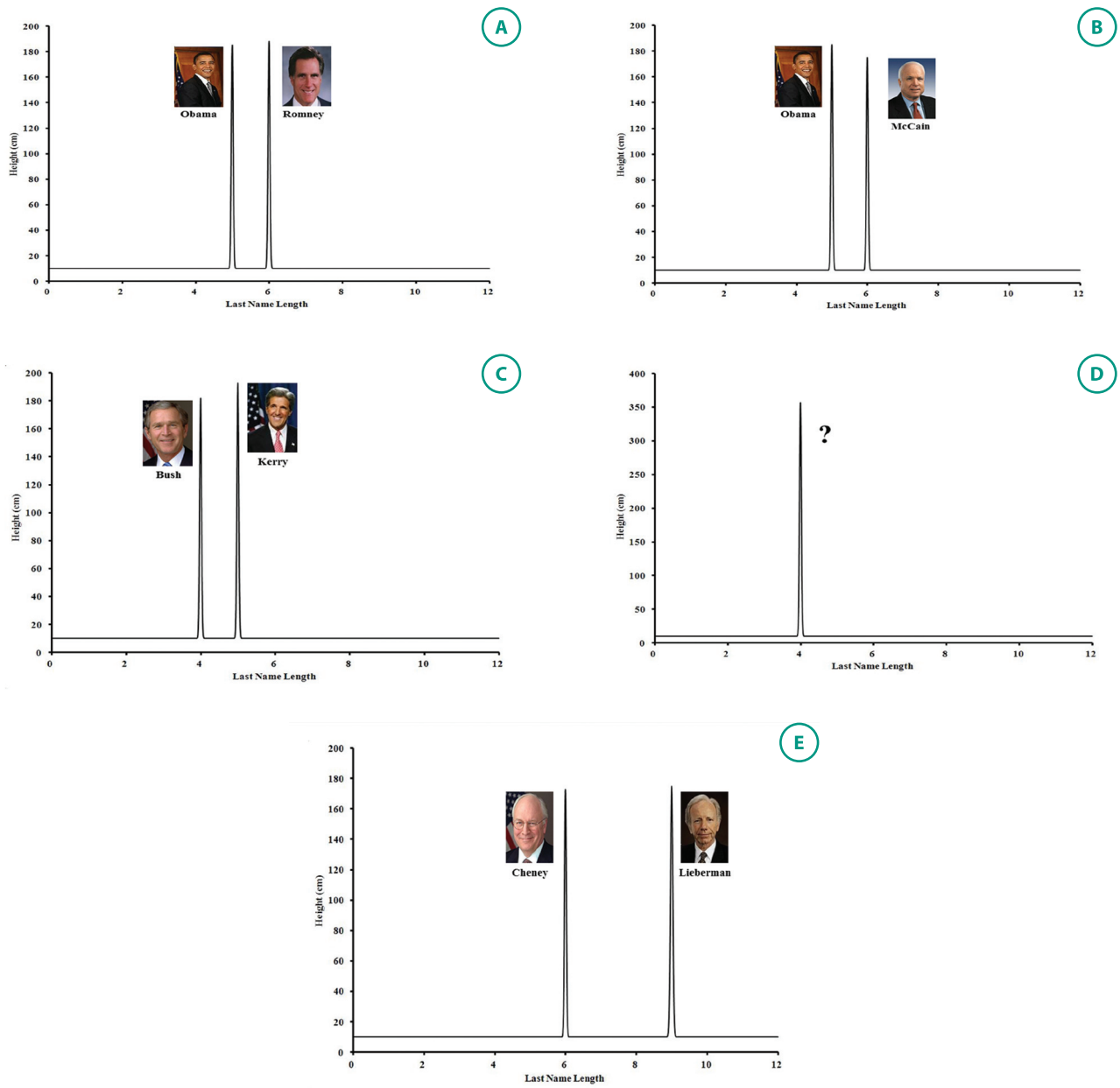



**Figure 6.** Namograms for simple mixtures. A. 2012 presidential election. B. 2008 presidential election. C. 2004 presidential election. D. 2000 presidential election. E. 2000 vice-presidential candidates.

a faster eluter than Lieberman (Gore's running mate) an explanation if found as to how Bush eventually won the the 2000 election (It is important to note that while our presidential prediction hypothesis is valid in this limited sample of presidential elections, it cannot be generalized to all presidential elections).

This example underscores the point that sample complexity is not only related to the number of compounds in a mixture, but is also impacted by the dimensionality of the sample[19] which was defined by Giddings as the number of distinguishable functionalities in a molecule. If two compounds share a number of structural properties between (such as chemical enantiomers) they may be just as difficult to separate than a set of 30 compounds with very different properties. As a result, there are limits to which the separation technique can resolve certain types of samples even when a number of different stationary phases are considered, and solutions to differentiate between sample components may require the use of a more powerful detector than an FID.

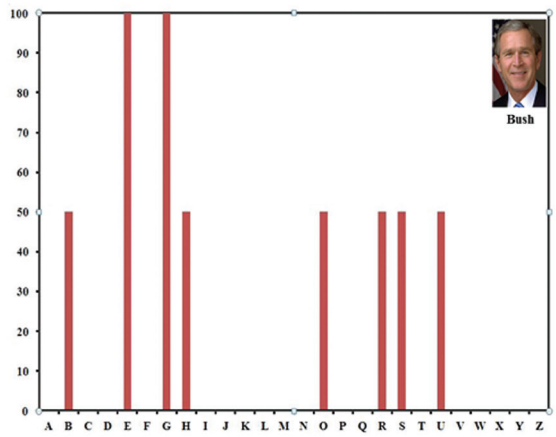
The co-elution of the Bush/Gore namogram peak can be elucidated in the alphabetography domain through a process called deconvolution, as shown in Figure 7. The alphabetogram that is produced by the co-eluting compounds is the sum of the profiles of the individual names, as shown in Figure 7A. This combined profile is then searched through the library of alphabetograms, which finds the name most similar to the combined profile, as shown in Figure 7B. The fact that the similarity index is not 1000 is an indication that the name is not "pure" and is combined with an "interferent". However, amongst the collection of names in the database, the profile of the co-eluents is still recognized as the closest to the combined profile. The top profile in the library is then subtracted from the combined alphabetogram, and the remaining profile is then re-analyzed in the library, the results of which produce a top hit for Gore with similarity index of 1000, signifying that all the compounds in the co-elution have been found. The more convoluted an alphabetogram profile is, the more difficult it becomes for the deconvolution process to resolve all the co-eluted compounds, but the capability to distinguish compounds in this domain is a welcome advantage to the combination of the two techniques.

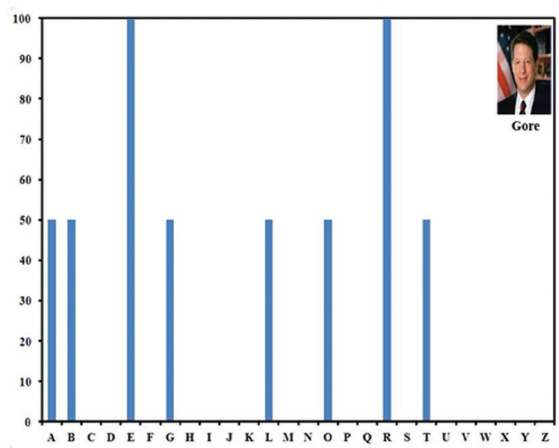
### 6.3. Complex Mixture Analysis

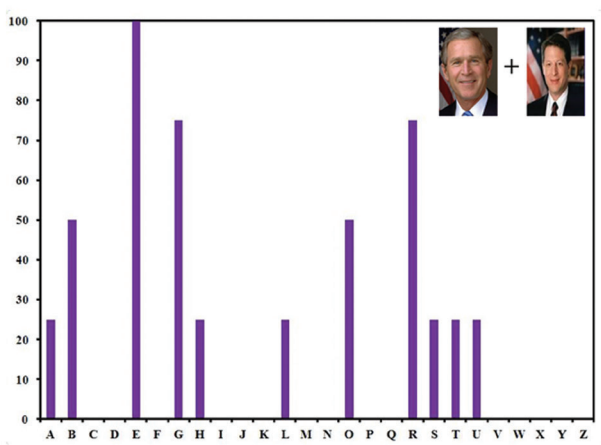
The impact of co-elutions is further explored in this section, and results are presented in Figure 8 for the separation of the sample of 44 US presidents. The 1D namograms by first and last name are overlayed to the surface plot in Figure 8A. These 1D namograms indicate a modest number of peaks resolved: 7 peaks for the first name separation (green) and 6 peaks for the last name separation (blue). A reasonable estimation of peak resolving power is the percentage of detected peaks relative to the number of sample components. This estimation can be done in this case because the total number of peak components is known, and provides a means for the comparison of different approaches to increase the resolving power of various separation strategies. The percentage of resolved peaks for the 1D namograms in Figure 8A are 15.9% and 13.6% for the first and last name respectively, and provides some insight into the resolution capabilities of one-dimensional separations that are consistent with results provided by chromatographic statistical overlap theory investigations[20,21].

One of the earlier methods to improve the resolution of a sample was the coupled-column (or tandem-column) technique[22], in which two-stationary phases are serially connected and sample components flow directly from the first stationary phase into the second stationary phase with no re-injection. Even though two stationary phases are utilized, this methodology is still a monodimensional separation technique because the two columns are not decoupled. The analogous setup in our example is a coupled namography system where the total name lengths (first and last name) are combined. The results of the coupled namogram system is able to increase the number of resolved names to 9 peaks (or 20.5% peak resolution). This separation represents an appreciable (albeit marginal) increase

A




B

| | Name | Similarity |
|---|---|---|
| Value | | |
| 1 | Bush, George | 923 |
| 2 | Bush, George | 923 |
| 3 | Hoover, Herbert | 878 |
| 4 | Roosevelt, Theodore | 875 |
| 5 | Washington, George | 853 |
| 6 | Hayes, Rutherford | 846 |
| 7 | Arthur, Chester | 846 |
| 8 | Cleveland, Grover | 833 |
| 9 | Cleveland, Grover | 833 |
| 10 | Grant, Ulysses | 827 |

**Figure 7.** Deconvolution procedure outline. A. Convolution of alphabetograms for co-eluting names. B. Library hit search of the convolved alphabetogram.

in separation capacity of the system, and suggests that coupled-column techniques can be used to extend the separation capabilities of a 1D system. However, it must also be recognized that there are limits to the separation power of 1D techniques that call for an increase in the dimensionality of the analyzer.

The comprehensive two-dimensional approach is clearly shown in the contour plot in Figure 8B. Even though two-dimensional GC employs a coupled-column arrangement, it is different from tandem-column GC because the two columns are decoupled at the interface. Discrete injections (or modulations) of the primary column effluent are sequentially introduced into the secondary column to produce a series of discrete chromatograms. As a result, each compound in the mixture now has a pair of retention markers, and the combined effect of two separation mechanisms provides more separation space, as shown in the both surface plot (Figure 8A) and the expanded contour plot (Figure 8B). A substantial increase in the number of peaks (22 peaks, or 50% peak resolution) is observed from this combination. In addition, the separation character of the two individual

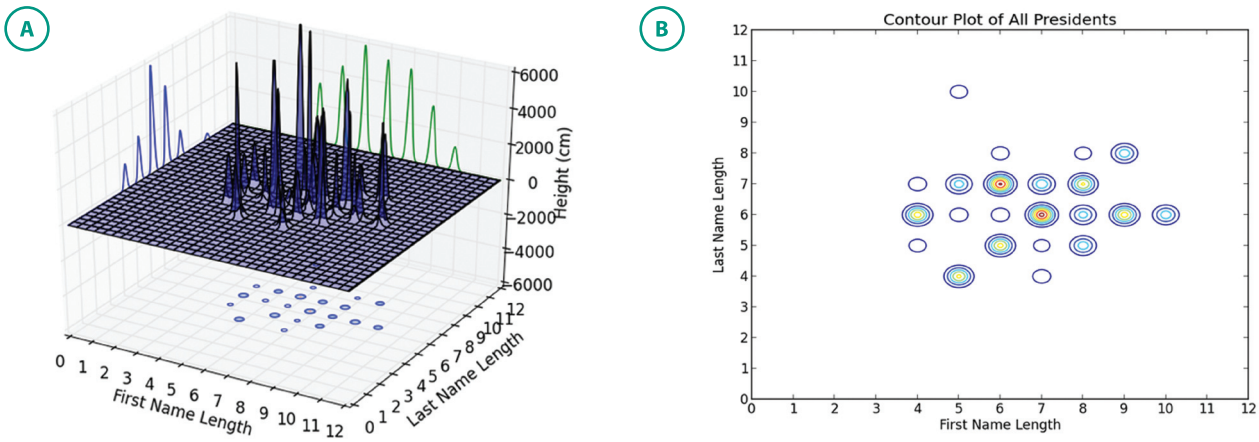



**Figure 8.** 2D Namogram of the 44 US presidents. A. Surface plot (with 1D projections and contour plot). B. Expanded contour plot.

mechanisms is preserved. Seven columns and 6 rows of peaks can be counted in Figure 8B, which correspond to the respective numbers of peaks obtained in the 1D namograms that were combined. The structured nature of these separations is very important, because it means that the peaks are not randomly spread in the two-dimensional plane, and that a thorough understanding of the separation gradients at play may provide the analyst with some very useful clues in deciphering the identity of the peak on the basis of its location in the separation space.

Even though the 2D contour plot in Figure 8B shows a substantial increase in resolving power when compared to 1D separations, it also shows that there are still a number of co-elutions due to the complexity of the sample. In order to further increase the peak resolution the alphabetogram of the coeluted peaks were deconvolved using the reiterative procedure outlined in section 3.2. The results of the deconvolution for the 2D namogram are outlined in Table 2. These results show a significant increase in the number of resolvable peaks when compared to single-channel (or FID) detection alone, and culminates in the resolution of over 90% of the names when using the 2D separation with multi-channel detection. The only 3 names that cannot be resolved in the 2D namogram/alphabetogram combination are names in the presidential list that appear in Table 1 more than once: John Adams (common name between the 2$^{nd}$ president and his son, the 6$^{th}$ president), George Bush (common name between the 41$^{st}$ president and his son, the 43$^{rd}$ president) and Grover Cleveland (the same person, but who appears twice on the list because he served non-consecutive 4-year terms as the 22$^{nd}$ and 24$^{th}$ president). Other samples have been used for this analogy besides the US presidents (names of the participants in our workshops, the names of the members of an academic department where a seminar is being presented, names of classroom students in a high-school or university setting, etc.), and the general trends reflected in Table 2 hold for sample sizes above 30 components.

**Table 2.** Overview of the Percentage of Resolved Peaks for 1D namography, coupled namography, and 2D namography.

| | Single-Channel Detector (FID) | Multi-Channel Detector (Alphabetography) with Deconvolution |
|---|---|---|
| Namography (First Name) | 7/44 (16%) | 18/44 (41%) |
| Namography (Last Name) | 6/44 (14%) | 13/44 (30%) |
| Coupled Namography | 9/44 (20%) | 21/44 (48%) |
| 2D Namography | 22/44 (50%) | 41/44 (93%) |

## 7. Conclusion

This example provides a surprisingly good number of opportunities to explain the concepts of gas chromatography, mass spectrometry and two-dimensional analysis. Like in many other analogies, some target concepts are not covered in the analog model. For instance, the chromatographic concepts of void time, peak band broadening, and analyte concentrations cannot be explained with this example. Likewise, the concept of molecular ions is not covered on the mass spectrometry side. However, some interesting questions regarding the potential need for additional chromatographic dimensions and their impact on the peak resolution can be addressed, and the question surrounding the minimum number of sample components beyond which a two-dimensional separation is a viable option could be worthy of further investigation. We intend to further refine/expand the analogy through interactions with interested users of the website software, which will hopefully help us to continue the fantastic teaching philosophies of Prof. Mc Nair.

## Acknowledgements

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***Artigos Originais*** de pesquisa: descrevem resultados de estudos completos. Deverão conter resultados de laboratório e/ou teóricos, que signifiquem uma contribuição expressiva para a área de técnicas de separação, seja ela conceitual, na instrumentação, ou na aplicação. Este tipo de contribuição é limitado a 6.000 palavras, incluindo as legendas das figuras e as referências, e no máximo 5 tabelas e/ou figuras **somados**. No momento do envio da prova de impressão, caso isto ocorra o autor será consultado se prefere revisar o artigo para enquadrá-lo em até 7 páginas, ou se prefere pagar as páginas excedentes. O número de páginas de um artigo depende muito das figuras e tabelas do mesmo. Este critério não é aplicado aos artigos convidados, cujo número de páginas será informado ao autor no momento do convite.

***Comunicações*** ("***Short Communication***"): são artigos completos, porém que relatam resultados mais curtos, oportunos, e/ou cuja relevância requer sua rápida publicação. Deverão ter a mesma qualidade dos artigos *Originais* porém, devido a seu caráter de comunicação preliminar, usualmente são de menor extensão. Este tipo de publicação deve ter no máximo quatro páginas impressas, incluindo todo o artigo, ou seja, tabelas, figuras e referências. O autor deve indicar claramente que se trata de uma comunicação no topo da primeira página do artigo.

***Artigos de Revisão*** crítica: revisões críticas sobre uma area específica das técnicas cromatográficas e relacionadas são também consideradas para publicação. Esses artigos devem se limitar a no máximo 10.000 palavras, incluindo as legendas, e até 10 tabelas e figuras **somadas**. Os artigos de Revisão Crítica deverão antes de sua submissão serem discutidos com um dos co-Editores mais relacionados ao assunto em questão. Artigos não encaminhados desta forma serão antes enviados a um co-Editor da área em que se enquadre para parecer e, somente então, serão enviados aos revisores, podendo atrasar significativamente sua publicação. Devem conter uma contribuição nova a respeito de um assunto de grande interesse atual, discutindo as vantagens e desvantagens do mesmo. O *Scientia* não publica apenas relato de artigos descritos na literatura, sem uma discussão crítica sobre os mesmos.

***Artigos de Alta Prioridade***: são publicados no primeiro número disponível do periódico, recebendo prioridade máxima de todo o sistema Editorial do periódico. Para justificar sua publicação como alta prioridade, os manuscritos deverão apresentar, de forma resumida, resultados importantes de recentes desenvolvimentos na área de cromatografia e técnicas relacionadas (espectrometria de massas, preparo de amostras, eletroforese capilar e outros). Não precisam conter resultados experimentais detalhados, sendo limitados a 2.500 palavras e três figuras e/ou tabelas **combinadas**.