Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography B, 822 (2005) 112–117
JOURNAL OF CHROMATOGRAPHY B
www.elsevier.com/locate/chromb

Preliminary investigation of using volatile organic compounds from human expired air, blood and urine for locating entrapped people in earthquakes

M. Statheropoulos [a], E. Sianos [a], A. Agapiou [a,*], A. Georgiadou [a], A. Pappa [a], N. Tzamtzis [a], H. Giotaki [b], C. Papageorgiou [c], D. Kolostoumbis [c]

[a] *National Technical University of Athens (NTUA), School of Chemical Engineering, Sector I, 9 Iroon Polytechniou Str., Athens 157 73, Greece*
[b] *Department of Nursing, TEI of Epirus, Ioannina, Greece*
[c] *Eginition Hospital, 74 Vass. Sophias Aven, Athens 115 28, Greece*

Received 14 December 2004; accepted 21 May 2005
Available online 29 June 2005

Abstract

A preliminary investigation on the possibility of using volatile organic compounds (VOCs) determination of expired air, blood and urine, for the early location of entrapped people in earthquakes, has been carried out. A group of 15 healthy subjects has been sampled. The identification of a common "core" of substances might provide indications of human presence that can be used for the development of a real time field analytical method for the on site detection of entrapped people. Expired air samples have been analyzed by thermal desorption GC/MS and VOCs from blood and urine by headspace SPME–GC/MS. Acetone was the only compound found common in all three matrices. Isoprene was found in both expired air and blood samples. Acetone and isoprene along with a number of saturated hydrocarbons were among the major constituents identified in expired air analysis. Various ketones (2-pentanone, 4-heptanone, 2-butanone) were also determined over urine specimens. Using the techniques and methods of field analytical chemistry and technology appears to be the proper approach for applying the results of the present study in real situations.

Keywords: Blood; Earthquakes; Entrapped people; Expired air; SPME; Thermal desorption; Urine; VOCs

1. Introduction

Volatile organic compounds (VOCs) analysis in expired air, blood and urine has been used for toxicological, medical, forensic, biochemical and other applications [1–6]. Some of these applications involve the correlation of VOCs with medical conditions of various groups of people, as well as, the correlation with biochemical processes and metabolism. As part of a project, which investigates the possibility of using VOCs present in expired air, blood and urine for locating entrapped people in an earthquake, an initial preliminary study has been carried out for the simultaneous detection of these compounds in all three matrices.

Normal human breath is known to contain a complex mixture of several hundred VOCs; more than 3000 different compounds have been observed in a study which involves breath analysis of 50 subjects [7]. Also, VOCs determination in plasma and urine has showed a broad number of compounds such as alcohols, aldeheydes, ketones, furans, pyrroles, terpenes, sulphur containing compounds, merkaptans, hydrocarbons and various heterocyclic compounds [8,9]. It should be noted that knowledge concerning the simultaneous determination of VOCs in expired air, blood and urine specimens of the same group of volunteers is limited and not much research work has been reported so far. The aim of this work is to investigate if a relatively small target group of compounds can be determined, preferably, in all three matrices (expired air, urine and blood), so as to eliminate the "overpopulation" of known compounds from the literature. The

* Corresponding author. Tel.: +30 210 7723109; fax: +30 210 7723188.
E-mail address: agapiou@central.ntua.gr (A. Agapiou).

1570-0232/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jchromb.2005.05.028

target is to determine, if possible, a core of substances that will act as a trace of the presence of a human being trapped under the ruins of a building.

In this work, Sorbent Tube sampling with thermal desorption GC/MS was used for the determination of VOCs found in expired air. In addition, headspace-solid phase micro extraction (HS-SPME)–GC/MS was applied for the analysis of VOCs evolved from urine and blood specimens. It should be emphasized that these methods are frequently referred in literature for this kind of analysis. They provide full mass spectra (chemical identification) that is used for identifying the type of compound in addition to its molecular weight and retention time. On the other hand, these methods are time-consuming limiting thus their real time application.

Other methods applied for the analysis of expired air include selected ion flow tube-mass spectrometry (SIFT-MS), proton transfer reaction-mass spectrometry (PTR-MS), membrane extraction with sorbent interface (MESI), ion mobility spectrometers (IMS) based methods, laser spectroscopy and non-specific sensor arrays technology (electronic noses) [10,11]. SIFT-MS provides low sensitivity (ppb) and is based on soft ionization mass spectrometry selectively applied in trace gases in expired air. It has very low time of analysis and uses three different chemical ionization agents (H_3O^+, NO^+, O_2^+). It requires minimum sample preparation and no separation of analytes [12]. PTR-MS can provide real time analysis and highly sensitive measurements for specific target VOCs although their identification is based on molecular mass and thus it is possible interferences from various molecular species to appear. Although it lacks chemical identification possibility, it requires no sample separation and it can be used for fast screening purposes based on molecular masses [13–15]. MESI is using a membrane that is selective for non-polar and volatile substances. It overcomes the usual problems in breath analysis (sample storage, high moisture, volatility) [16]. IMS is a low cost, portable (even miniaturized) device appropriate for field breath analysis. It has very low sensitivity, which can be improved by using different carrier gases [17]. Laser spectroscopy has also been referred in measuring ethane in exhaled air at ppt range [18]. Electronic noses with current technology need preconcentration, as well as chemometric processing which is available mostly in exploratory mode, not fully automated [19].

It should be noted that the study presented in this paper, is a starting point for the whole project, which exhibits complexity because the medical conditions of entrapped people resembles to that of fasting, stressed and heavily injured. Furthermore, the detection process needs to be modeled on the side of mass transfer of VOCs derived from breath and body fluids to the sampling device. Following this need for initial results, all the analyses have been done with the help of healthy volunteers, which has been verified by standard biochemical tests not showing pathological values.

Regardless of the analytical and sampling compromises that have to be made for the initial results, the project is focused on entrapped people and for this reason all the SPME analyses have been done without any pretreatment in order to produce the maximum yield of VOCs (addition of salts, adjustment of pH, heating and agitation) [20,21]. Following this need, the urine and blood samples have been analyzed within 24 h from the collection time, so as artifacts from sample degradation not to be measured. To achieve fast analysis, the sampling procedure has been split in 3 days, in order to reduce the sample flow of samples to the lab to one-third per day, which is sufficiently low for almost immediate analysis.

2. Experimental

2.1. Human subjects

Fifteen healthy volunteers were selected, comprising 10 males (mean age 33) and 5 females (mean age 28). All subjects have signed a voluntary participation statement and have been informed about the terms of the Hawaii declaration on “Ethics protocol on medical experiments”. The protocol for the preparation of the volunteers was as presented in [22].

2.2. Expired air sampling

Expired air was chosen to be sampled in 5 l Tedlar bags. All volunteers were asked to blow calmly air into the Tedlar bag by mouth, while inspiring from the nose. Three-layer sampling tubes have been chosen (TD-300, Alltech) due to the high diversity of structure and molecular weight of the compounds expected to be analyzed. The 6 mm o.d., 115 mm length tubes consisted of 300 mg Carbograph2, 200 mg Carbograph 1 and 125 mg Carbosieve S-III layers. All sampling tubes were conditioned for 2 h, at 300 °C and at a flow of 150 ml min^{-1} of He, in order to minimize background effects and spiked with 1 μl liquid volume of 50 mmol l^{-1} methanolic solution of chlorobenzene-D5 (ISTD).

The air from the bag was pumped through the sampling tube, with the use of a sampling pump (VSS-1, A.P. Buck, USA). The removal of air was carried out using constant-flow mode (the VSS-1 pump automatically adjusted the pressure gradient to obtain selected flow) at 200 ml min^{-1}. Blank ambient air samples were taken from the sampling location. In order to preserve sample integrity, the VOC content of the air in Tedlar bags was, immediately, transferred to the sorbent sampling tubes.

The in-house made sorbent desorption system has been thoroughly tested and its performance has been evaluated before the analysis of this work. Evaluation procedures for the cryo trap total condensation ability and sorbent tube thermal desorption duration were applied. Furthermore, evaluation procedures on sorbent trapping efficiency were also performed on the system. Detection limit for hexane was found to be lower than 10 ng, when the system worked as an injector. System linearity exhibited r^2 value of 0.986 for calibration curves at nanogram to low microgram region and value 0.943 for microgram to low milligram mass region. Reproducibility

experiments by injecting 2 μl of 0.001% hexane in toluene solution showed R.S.D. of 5.24%.

2.3. Expired air VOCs chromatographic analysis

Sorbent tubes were thermally desorbed to a HP 5890/5972 GC/MS (Agilent Technologies) system, using an in house made thermal desorption unit (TDU). Other than the thermal desorption module it includes a refocusing trap based on freezing with liquid nitrogen, in order to enhance the chromatographic separation. System's schematic drawing is shown is Fig. 1.

Desorption flow of He has been set to 30 ml min^{-1}, while the temperature was kept constant at 200 °C. Desorption and refocusing duration was 20 min in order to ensure 100% recovery of sorbent-trapped analytes. The cryo trap capillary was a 22 cm part of a 0.53 mm i.d., AT-Q PLOT column (Alltech) and it was chosen in order to enhance trapping of highly volatile VOCs, as shown in literature [23]. A 20 s heating pulse has proved to be adequate for flash desorption of trapped analytes into the GC column.

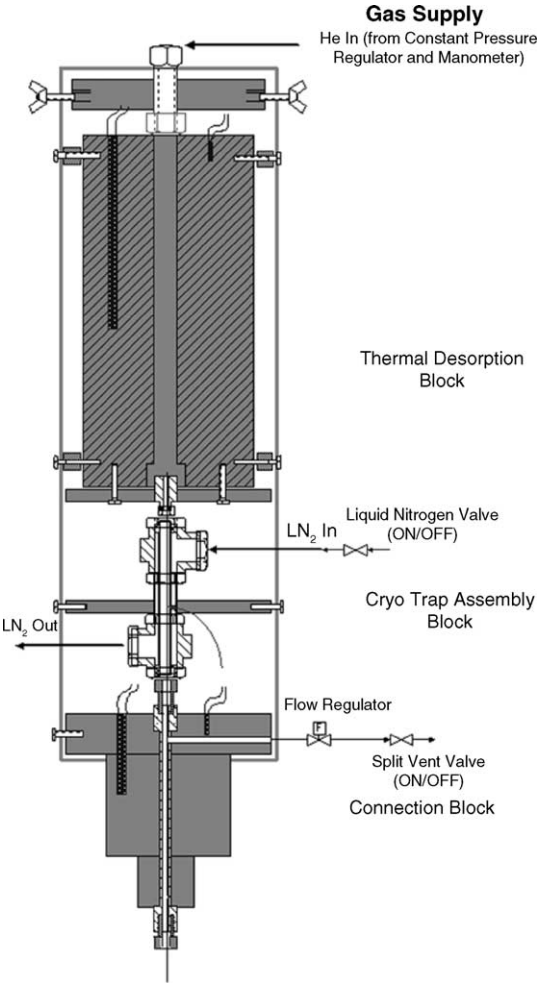

Fig. 1. Drawing of the in-house made TDU.

A 60 m SPB-624 capillary column with 1.4 μm stationary phase and internal diameter of 0.25 mm (Supelco) has been utilized for high-resolution chromatographic separation. Column head pressure of helium purge gas has been set to 25 psi. GC program has been selected as follows: 35 °C initial for 5 min, ramp of 4 °C min^{-1} up to 180 °C, holds for 20 min. MSD mass range has been limited to 42–350 amu range due to the expected detection of VOCs, but with a benefit of 1.8 scan s^{-1}.

2.4. Expired air VOCs quantification method

Chromatographic peaks have been identified with the help of Wiley 138 mass spectrum library, using similarity indexes higher than 70%. Quantitative results were generated with the application of internal standard method [24], using the following equation:

$$C_i = \frac{A_i}{A_{ISTD}} \frac{1}{RRF_i} C_{ISTD}$$

where C_i is the concentration of the substance i in the vapor phase expressed in nmol l^{-1} of expired air; A_i the peak area of substance i, in counts; A_{ISTD} the peak area of internal standard, in counts; RRF_i the response factor of substance i, relative to chlorobenzene-d5, which expresses the different ionization of the substance i compared to the internal standard; and C_{ISTD} is the calculated concentration of internal standard in the total air volume sampled in nmol l^{-1}.

The concentration calculation for the internal standard has been done by reducing the known molar quantity injected on the tube to the 5 l of air sampled from the Tedlar bags. This concentration is calculated to be equal to 10 nmol l^{-1}.

2.5. Blood and urine sampling

All blood and urine samples have been collected immediately after giving samples of expired air, at the medical laboratory of Aiginiteion Hospital of Athens, Greece, under the same conditions a typical medical examination would require. Two duplicate samples of 5 ml for each blood and urine were collected. Each sample was placed immediately to 15 ml vials and capped firmly (15 ml vials, with an open top screw cap type 18/400 sealed with TFE/silicon liners type 18/400, 10/50 mil, supplied by Alltech). One sample of the duplicate pairs was transferred to a deep-freezer for storage and future confirmation use and the other sample to the lab for analysis.

The volunteers were divided in three groups and followed the sampling procedure at sequential days, in order to reduce the sample flow in the analytical laboratory to 10 per day (five blood and five urine). All blood and urine samples along with their water blanks (one each day) were analyzed for headspace VOCs within 20 h from collection time.

2.6. Urine and blood VOCs chromatographic analysis

All urine and blood VOCs analysis have been performed with 85 μm carboxen/polydimethylsiloxane (PDMS) on a StableFlex SPME fiber, supplied by Supelco. The SPME needle holder pierced the TFE/silicon vial seal and the fiber was exposed to the headspace vapor for 30 min. Samples brought to the lab have been injected with 0.5 μl of methanolic mixture containing 50 mmol l^{-1} chlorobenzene-D5, used as internal standard (IT-Chem, Hellas) and have been left to equilibrate for 30 min prior to SPME sampling.

Desorption of VOCs from the SPME fiber has been carried out at the heated split/splitless injection port of a HP5890 GC coupled by a HP 5972 MSD (Agilent Technologies). Injection port temperature has been kept constant at 220 °C and its mode of operation has been selected to be splitless during fiber exposure in the heated zone and switched to injector purge mode (split) at 4 min run time. Injector flow has been set to 30 ml min^{-1}. The set of GC/MS instrumental parameters has been kept identical with the expired air analysis one, in order to produce comparable results. Only the electron multiplier voltage has been set to 200 V higher than the autotune value in order to enhance the detection ability of the MSD. Substances have been identified using the same procedure with the expired air VOCs analysis.

3. Results and discussion

3.1. Expired air VOCs

Breathing is known to be a dynamic process and VOCs detected are continuously changing according to the physical and physiological status and the current environment of the person examined. In order to ensure the "physiological" status of each of the subjects biochemical tests have been conducted. These included 63 different medical parameters to be measured (e.g. cholesterol levels, sugars, white blood cells) and psychological profiling. In order to eliminate the environmental VOCs effect, the subjects were asked to stay for 1 h in the same room that had previously been sampled for atmospheric VOCs. Each substance detected in the expired air sample was compared to the room "blank" sample and only the substances with concentrations over three times higher than the blank were reported. A typical chromatogram of expired air analysis is presented in Fig. 2.

VOCs expired air analyses for the 15 volunteers resulted in 63 VOCs to be identified including hydrocarbons, alcohols, ketones, aldeheydes, acids, esters, chlorinated hydrocarbons, aromatics and heterocyclic compounds. The expected "core" of VOCs that may lead to a "human trace" are shown in Table 1. Table 1 presents indicative median concentrations of VOCs found in expired air samples showing more than 80% appearance in the human subjects and their median concentration. The fourth column presents the relative concentration of each of the substances if compared to the concentration of acetone (substance-to-acetone ratio, STA ratio). Six substances were found to be common in all the samples examined: isoprene, acetone, pentane 2-methyl, 1-pentene 2-methyl, hexane, and hexane 3-methyl while other seven showed more than 80% appearance. These substances are showing STA ratio over or close to 15 and 100% appearance in all samples.

Table 1
VOCs identified in expired air

Compound	Indicative median concentration (nmol l^{-1})	Appearance (%)	Relative response to acetone (%)
Acetone	11.7	100	100
Pentane, 2-methyl	6.81	100	58.2
Hexane	6.22	100	53.2
Isoprene	3.91	100	33.4
1-Pentene, 2-methyl	3.16	100	27.0
Hexane, 3-methyl	1.99	100	17.0
Methane, chloro-	1.39	93	11.9
Benzene	1.35	93	11.5
Heptane, 2,4-dimethyl	1.07	93	9.14
Hexane, 2-methyl	0.98	87	8.38
Acetaldeheyde	0.92	93	7.86
Hexane, 2,3-dimethyl	0.56	87	4.79
Alpha pinene	0.05	87	0.43

The VOCs median concentration findings obtained from this study such as acetone (11.7 nmol l^{-1}) and isoprene (3.91 nmol l^{-1}) have showed agreement with previous reports referring values of 10–48.4 nmol l^{-1} for acetone [25] and 1.60–10.3 nmol l^{-1} for isoprene [1]. Alternatively, acetone content given by other authors has presented mean values of 38 or 18.9 nmol l^{-1} [26,27] and for isoprene 14.5 or 48.5 nmol l^{-1} [28,29]. Although ethanol and pentane showed slightly lower appearance below 80%, their STA ratio should not be overlooked (median concentrations of 5.32 and 1.65 nmol l^{-1} and STA ratios of 45.3 and 14.1%, respectively, for ethanol and pentane), as they are considered among the main VOCs of human breath. The levels of hydrocarbons identified were not expected. Exhaled hydrocarbons are correlated with lipid peroxidation and the possible explanation is that volunteers were asked to follow a certain preparation protocol. For further testing the repeatability, thermal desorption system stability and within person variability, an examination on three samples of the same individual was carried out. The results defined that the number of the VOCs identified were analogous for each measurement for over 97%, whereas the within-individual variability was found 70%.

3.2. Urine and blood VOCs

The total number of substances identified for blood and urine, is 46 and 38, respectively. Chemically, they show the same diversity as those of expired air including hydrocarbons, alcohols, ketones, aldeheydes, sulphides and heterocyclic compounds. Results for blood VOCs common in all samples or with appearance over 80% ("core substances") are shown

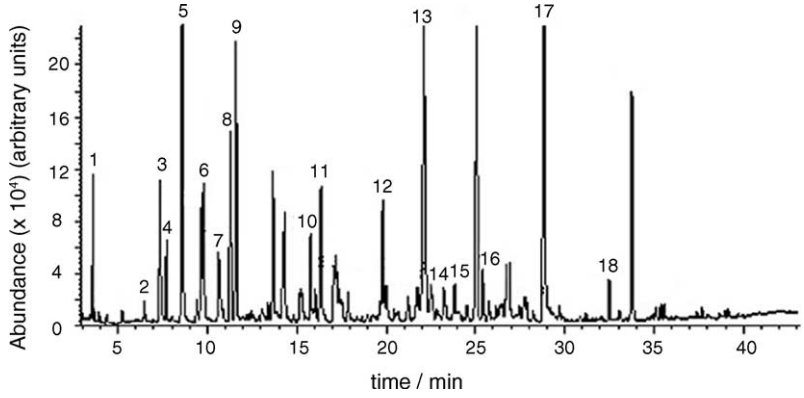

Fig. 2. Typical chromatogram obtained by an expired air test measurement. Compounds detected: (1) chloro methane, (2) pentane, (3) isoprene, (4) ethanol, (5) acetone, (6) 2-methyl pentane, (7) 3-methyl pentane, (8) 2-methyl pent-1-ene, (9) hexane, (10) 2-methyl hexane, (11) 3-methyl hexane, (12) acetic acid, (13) 4-methyl heptane, (14) 1,2-dimethyl-trans cyclohexane, (15) toluene, (16) 2,4-dimethyl heptane, (17) d_5-chlorobenzene—internal standard, and (18) alpha pinene. Sampling and chromatographic conditions are given in the text.

Table 2
VOCs identified in the air phase of blood samples

VOCs	Appearance (%)	Relative response to acetone (%)
Acetone	100	100
Isoprene	87	4.60
Butane, 2,2,3,3-tetramethyl	100	0.45
Toluene	100	0.24
Phenol	80	0.21

on Table 2. Only three substances were identified in all samples: acetone, butane 2,2,3,3-tetramethyl and toluene while isoprene and phenol show the higher tendency of existing in all samples. However, STA ratio results using the amount of those substances collected on the SPME needle looks promising only for acetone–isoprene pair. The other substances have been detected, but with low STA ratio.

"Core" substances for human urine are summarized in Table 3. Those with 100% appearance are five: acetone, hexane 2,2-dimethyl, toluene, 1H-pyrrole and *p*-xylene. Moreover, ethanol, 2-butanone, benzene, 2-pentanone, 4-heptanone and phenol were identified over 80% in samples examined. Significant responses compared to that of acetone, with STA ratio over 5%, have been observed for the ketone part of the substances detected, while the hydrocarbon portion is detected in very low STAs.

Table 3
VOCs identified in the air phase of urine samples

VOCs	Appearance (%)	Relative response to acetone (%)
Acetone	100	100
2-Pentanone	87	15.3
4-Heptanone	87	6.86
1H-pyrrole	100	6.37
2-Butanone	87	2.80
Toluene	100	2.60
Benzene	93	1.31
Ethanol	87	1.20
Hexane 2,2-dimethyl	100	1.01
p-Xylene	100	0.39
Phenol	87	0.28

The stability of the results and method repeatability was tested by examining duplicate samples stored in deep freezing. Blood and urine samples of three individuals (duplicates) were analyzed after 30 days of storage. It has been reported that all chemical in urine specimens are stable in −20 °C storage conditions, up to 2 months [30]. These results were compared with the initial results for the three subjects. The observations that have been made, pointed out analogous results for urine and blood samples of the three subjects at 90 and 80%, respectively.

The findings, presented in Tables 2 and 3, suggest that there is a variation among the volatiles of the vapor phase in blood and urine samples, among different individuals, as it has been already reported [8]. It is characteristic that three of the 46 compounds identified in blood are common for all the subjects and five out of 38 in urine. However, VOCs in urine samples of the volunteers seem to have less variation compared to blood samples. It appears that 13 of 38 compounds in urine were identified in over 80% of the samples and 18 in over 50% (not shown on Tables 2 and 3). In blood five compounds were present in over 80% of the samples and seven compounds over 50%.

4. Conclusions

Human expiration is a continuous function so the main part of VOCs detected from entrapped people in an instance of an earthquake is expected to come from it. Acetone has been found to be present in all three matrices (expired air, blood and urine) so the response to the analytical device is thought to be cumulative and this substance is expected to be the first one detected when measuring under ruins. Moreover, the verification of human presence can be enhanced by the detection of isoprene (found in both expired air and urine) at STA ratios close to 10–30%. Finally, the six compound core,

found in expired air, and the STA ratios of each substance can be used as a starting point for the construction of the on-site detection method.

Ketone content of air sampled under building ruins can alternatively be used for the detection of entrapped people as urine analysis showed. The expected concentration of ketones is estimated to be low, even at trace amounts, because humans produce limited amounts of urine and the dehydrated states when entrapped are expected to minimize urine production. However, every one of the substances detected and shown on Tables 1–3 may be specific enough to imply the presence of a human being if they are not found in normal indoor air or they are not produced by other background sources.

Human "odor", regarding VOCs, has been used in search and rescue operations, as dogs have been used to detect earthquake victims ever since organized rescue services were instated. However, the analytical findings of this feasibility study have been obtained by time-consuming laboratory based methods. Consequently, the employing of field chemical analysis and technology which utilizes portable and mobile instruments for direct measurements in time and space ought to be investigated [31]. Portable sensors and instruments (e.g. MS-based systems) or electronic noses might prove appropriate for this purpose. The introduction of chemical analysis in physical catastrophes may prove effective in early location of entrapped people.

5. Future works

The research project is planned to continue measuring more parameters of the detection procedure. Human disorders in metabolism when entrapped are known to resemble to states of fasting or extremely stressed. Also, measurements on sick or multi-injured persons can produce valuable data on the VOCs detected after some hours or days following the earthquake.

Dead humans or even dead animals can produce background VOCs that may be common with those of living people making the detection method hard to distinguish [32]. Other parameters that are possible to inhibit VOC detection, in an earthquake, are environmental background substances (e.g. indoor or outdoor air), particulate matter, VOCs from construction materials, broken pipes, plants and entrapped animals. All of these background sources will be the focus of future investigations.

Acknowledgements

This study is part of a project, financially supported by the Greek Earthquake Planning and Protection Organization and the General Secretariat of Research and Technology, PENED 2001. The authors acknowledge the support of Mrs. C. Nikolaou (Assistant Professor in National and Kapodistrian University of Athens, Department of Medicine) for the overall supervision of the clinical tests, carried out at Biochemical Analytical Laboratory of "Aiginiteion" Hospital of Athens.

References

[1] S. Mendris, P.A. Sobotka, D.E. Euler, Free Radiat. Res. 23 (1995) 117.
[2] S.K. Kundu, J.A. Bruzek, R. Nair, A.M. Judillay, Clin. Chem. 39 (1993) 87.
[3] A.W. Jones, Clin. Chim. Acta 146 (1985) 175.
[4] A. Manolis, L.J. Burney, B.A. Bobbie, Clin. Biochem. 16 (1983) 229.
[5] L. Junting, C. Peng, O. Suzuki, Forensic Sci. Int. 97 (1998) 93.
[6] G.A. Mills, V. Walker, J. Chromatogr. A 902 (2000) 267.
[7] M. Phillips, J. Herrera, S. Krishman, M. Zain, J. Greenberg, R.N. Cataneo, J. Chromatogr. B 729 (1999) 75.
[8] A. Zlatkis, R.S. Brazell, C.F. Poole, Clin. Chem. 27/6 (1981) 789.
[9] H.G. Wahl, A. Hoffmann, D. Luft, H.M. Liebich, J. Chromatogr. A 847 (1999) 117.
[10] N. Teshima, J. Li, K. Toda, P.K. Dasgupta, Anal. Chim. Acta 535 (2005) 189.
[11] W. Miekisch, J.K. Schubert, G.F.E. Noeldge-Schomburg, Clin. Chim. Acta 347 (2004) 25.
[12] D. Smith, P. Spanel, S. Davies, J. Appl. Physiol. 87 (1999) 1584.
[13] B. Moser, F. Bodrogi, G. Eibl, M. Lechner, J. Rieder, P. Lirk, Respir. Physiol. Neurobiol. 145 (2005) 295.
[14] A. Amann, G. Poupart, S. Telser, M. Ledochowski, A. Schmid, S. Mechtcheriacov, Int. J. Mass Spectrom. 239 (2004) 227.
[15] P. Lirk, F. Bodrogi, J. Rieder, Int. J. Mass Spectrom. 239 (2004) 221.
[16] H. Lord, Y. Yu, A. Segal, J. Pawliszyn, Anal. Chem. 74 (2002) 5650.
[17] V. Ruzsanyi, J.I. Baumbach, S. Sielemann, P. Litterst, M. Westhoff, L. Freitag, J. Chromatogr. A, in press.
[18] H. Dahnke, D. Kleine, P. Hering, M. Murtz, Appl. Phys. B 72 (2001) 971.
[19] C.D. Natale, A. Macagnano, E. Martinelli, R. Paolesse, G. D'Arcangelo, C. Roscioni, A.F. Agro, A. D'Amico, Biosens. Bioelectr. 18 (2003) 1209.
[20] G.A. Mills, V. Walker, J. Chromatogr. B 753 (2001) 259.
[21] G.A. Mills, V. Walker, H. Mughal, J. Chromatogr. B 723 (1999) 281.
[22] B. Krotoszynski, G. Gabriel, H. O'Neil, J. Chromatogr. Sci. 15 (1977) 239.
[23] A.J. Bordening, C.W. Wilkerson, Anal. Chem. 68 (1996) 2874.
[24] W.A. McClenny, M.W. Holdren, Compendium of methods for the determination of toxic compounds in ambient air, Method TO-15, Determination of volatile organic compounds (VOCs) in air collected in specially-prepared canisters and analyzed by gas chromatography/mass spectrometry, EPA, Cincinnati, 1997.
[25] M. Phillips, J. Greenberg, J. Chromatogr. B 422 (1987) 235.
[26] C. Grote, J. Pawliszyn, Anal. Chem. 69 (1997) 587.
[27] A.W. Jones, J. Anal. Toxicol. 9 (1985) 246.
[28] M. Phillips, M. Sabas, J. Greenberg, Am. J. Clin. Pathol. 46 (1993) 861.
[29] A. Cailleux, X. Moreau, A. Delhumeau, P. Allain, Biochem. Med. Metab. Biol. 49 (1993) 321.
[30] S. Fustinoni, R. Giampiccolo, S. Pulvirenti, M. Buratti, A. Colombi, J. Chromatogr. B 723 (1999) 105.
[31] G. Matz, W. Schroder, A. Harder, A. Schillings, P. Rechenbach, Field Anal. Chem. Technol. 1 (1997) 181.
[32] M. Statheropoulos, C. Spiliopoulou, A. Agapiou, Forensic Sci. Int., in press.