

OPTIMIZATION OF ORGANOMETALLIC COMPOUNDS EXTRACTION
FROM AQUEOUS SAMPLES IN ORDER TO IMPROVE THEIR GAS
CHROMATOGRAPHY-MASS SPECTROMETRY ANALYSIS
PERFORMANCE*

M. H. KOVACS¹, D. RISTOIU¹, C. VOICA¹, T. RISTOIU³

¹Babes Bolyai University, Environmental Science and Engineering Faculty, Fintinele 30 Str.,
Cluj-Napoca, 400294, Romania

²National Institute for R&D of Isotopic and Molecular Technologies - 71-103 Donath Str.,
Cluj-Napoca, 400293, Romania

³Technical University, Constantin Daicoviciu 15 Str, Cluj-Napoca, 400020, Romania
E-mail: haydee_kovacs@yahoo.com

Received September 5, 2011

Concerns regarding organometallic compounds are given by their properties as toxicity, bioavailability and mobility through different environmental compartment. Therefore improvement of their quantitative analysis from environmental matrix as water continues to be an important topic for analytical research. In this work *solid phase microextraction* (SPME) combined with *headspace extraction* (HSE) and *liquid-liquid extraction* (LLE) of multielemental speciation of organometallic compounds from water samples was mended in order to smooth their analysis through gas chromatography-quadrupole mass spectrometric technique (GC-qMS). Increases of organometallic compounds extraction recovery (88–116 %) was obtained through ethylation and simultaneous HS-SPME extraction of derivative compounds followed by GC-MS analysis. The main experimental parameters which influenced significantly the extraction efficiency of organometallic compounds through this method were fiber type, derivatization agent, extraction and desorption time as well extraction and desorption temperature. The analytical feature of the HS-SPME-GC-MS method was evaluated. Optimization of this technique allowed attaining of lower limits of detection (12–56 ng·L⁻¹) without alteration of linearity (15 ng·L⁻¹– 100 µg·L⁻¹, n = 9). Through this proposed method good linear regression ($n \geq 0.9950$) and repeatability was obtained. Optimization of this method allowed the evidence of compounds as organolead, organotin and organomercury in Someş River basin between ranges of 0.5–2.65 µg·L⁻¹, 25 – 98 ng·L⁻¹ and 22 ng·L⁻¹ – 0.9 µg·L⁻¹, respectively.

Key words: organometallic compounds, HS-SPME extraction, GC-MS, surface water.

* Paper presented at the 12th International Balkan Workshop on Applied Physics, July 6–8, 2011, Constanta, Romania.

1. INTRODUCTION

Concerns regarding the presence of organometallic compounds in surrounding environment are caused by their toxicity and bioavailability [1]. Their presence in environment could be explained once through direct discharge which is mainly linked to human activity and secondly by the bioconversion of the inorganic contaminants, process which is induced by biota [2].

Unfortunately these organometallic compounds are mobile in the biosphere and continue to undergo to several biogeochemical cycles throughout they suffer continuous changes in their structure and properties, resulting in formation of more organometallic species [3].

Considering their extensive presence in all environmental media as well their adverse effects on human health and biota, their quantitative and qualitative determination from complex environmental matrix has become more interested [5].

Unfortunately their determination from environmental matrices as well biological matrices are extremely difficult owing to their matrix effects and presence in low amount in the sample [6, 7]. Therefore in order to perform their analysis is important to establish adequate extraction, preconcentration and separation methods.

The most important organometallic compounds owing to their extensive abundance in almost all environmental media as well to their increased ecotoxic properties are organomercury, organolead and organotin species [8].

2. EXPERIMENTAL

2.1. MATERIALS AND REAGENTS

Organic species of tin as *monobutyltin trichloride* (MBT), *dibutyltin dichloride* (DBT) and *tributyltin chloride* (TBT) were purchased from Sigma-Aldrich, Germany. Organic forms of lead as *trimethyllead chloride* (TML) and *triethyllead chloride* (TEL) were also getting from Sigma-Aldrich, Germany while organic species of mercury, including methylmercury chloride (MeHg) and mercury (II) nitrate were obtained from Merck, Germany. All other used chemicals and solvents were analytical-reagent grade.

2.2. SAMPLING CONDITION

Surface water samples were collected in polyethylene bottles excepting cases when organic mercury species were the target analytes, case in that samples were collected in Teflon containers in order to avoid metallic compounds reaction with bottle surface. Before all sampling campaign the sampling bottles were subjected to

acid cleaning with HNO_3 in order to remove possible metal impurities from the bottles wall and to prevent further metal adsorption. All samples were stored in dark at 4 °C until analysis.

2.3. INSTRUMENT

Gas chromatographic equipment engaged with a quadrupole mass spectrometer detector, Thermo Electron Corporation product, was used in order to perform the analysis of organometallic species. An automated headspace-solid phase microextraction device, Thermo Electron Corporation product, was employed to perform these species extraction from water matrices.

SPME extraction optimizations of proposed organometallic compounds were performed on polydimethylsiloxane fiber (PDMS) with 100 and 30 μm thickness, respectively, and with divinylbenzene/carboxen/polydimethylsiloxane fiber (DVB/CAR/PDMS) with 50 μm /30 μm thickness. All fibers were conditioned before use, according to instructions of manufacturer. Conditioning process involved heating of fiber in the chromatographic injection port of the instrument at 250 – 270 °C (depending on fiber type) between 1 – 6 h time period, depending also by fiber type. Splitless mode of split/splitless injector (2 mm i.d. glass liner) was used in order to perform the analysis. Target organometallic compounds separation was obtained using a TR-5MS (5 % phenyl/methylsiloxane) fused-silica column with 30 m length, 0.25 mm i.d. and 0.25 μm film thickness. Used column temperature started from 40 °C which was maintained constant for 3 minutes, followed by an 20 °C $\cdot\text{min}^{-1}$ increasing program until 250 °C, which was maintained constant for 5 minutes. As carrier gas, helium was used with the following flow rate: 0.9 mL $\cdot\text{min}^{-1}$ for 7 minutes time period, followed than by a 1.2 mL $\cdot\text{min}^{-1}$ flow rate which was maintained for the rest of the analysis time. The quadrupole mass spectrometer detector transfer line and ion source temperatures were set at 250 and 200 °C, respectively in all analysis case. Electron impact ionization (EI) mode was used with 70 eV electron energy. In case of full scan mode the mass range was set between 40 – 500 m/z, while in case of selective ion monitoring (SIM) mode the target masses were: 217, 246 m/z for methylmercury; 223, 253 m/z for inorganic mercury; 231, 260 m/z for trimethyllead; 237, 295 m/z for triethyllead; 179, 235 m/z for monobutyltin and 149, 179 m/z for dibutyltin as well for tributyltin.

3. RESULTS AND DISCUSSIONS

3.1. DERIVATIZATION PROCESS OPTIMIZATION

Most of organometallic compounds are polar compounds than nonpolar compounds, therefore in order to could perform their chromatographic analysis is necessary to be derivatized prior analysis.

In this case derivatization process was performed using NaBEt_4 . Evaluation of pH influence on derivatization efficiency was evaluated and results showed highest derivatization yields for all compounds at 5 pH – see Fig. 1.

3.2. ORGANOMETALLIC COMPOUNDS EXTRACTION OPTIMIZATION

As regards liquid-liquid extraction, good limits of recoveries and reproducibility were obtained in case of extraction with hexane than in case of isoctane – see Fig. 2.

In some cases during extraction process emulsion are formed which make compounds separation more difficult. According of this problem could be done by sample acidification with HCl followed by its centrifugation with 6500 rpm for 5 minutes.

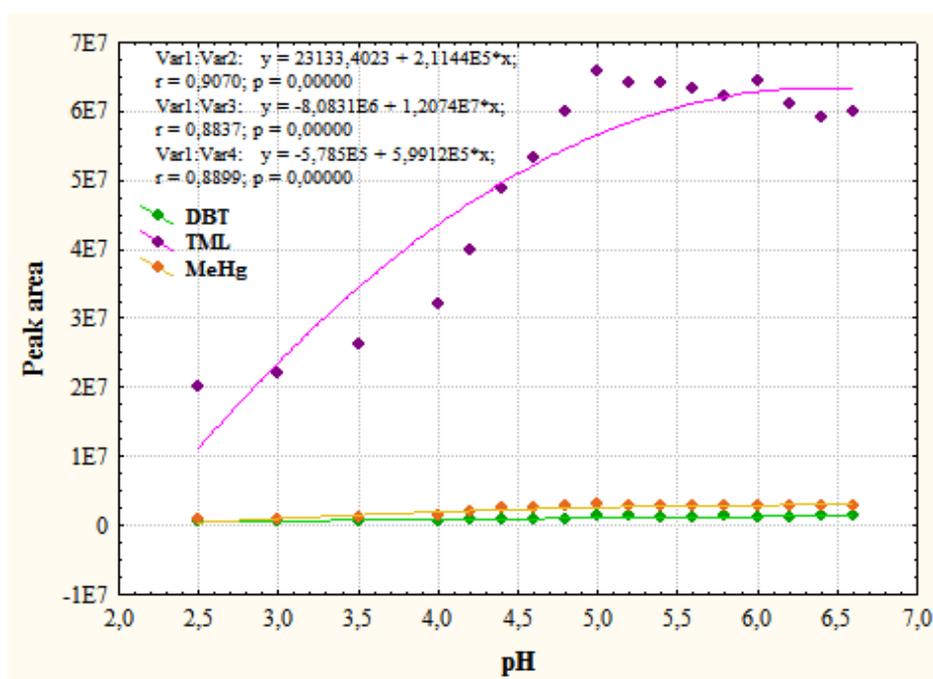


Fig. 1 – pH influence on derivatisation efficiency.

In case of HS-SPME extraction, 10 mL of water sample which contain 0.8 acetate buffer solution (to achieve 5 pH) and 45 μL of 5 % (w/v) of NaBEt_4 was placed in glass vials and closed as sun as possible with PTFE-coated silicon rubber septum. The vials were exposed to heat in order to allow headspace extraction. Good responses were obtained in case of heating exposure at 95 °C for 25 minutes time period under dynamic condition (stirring) for all organometallic compounds.

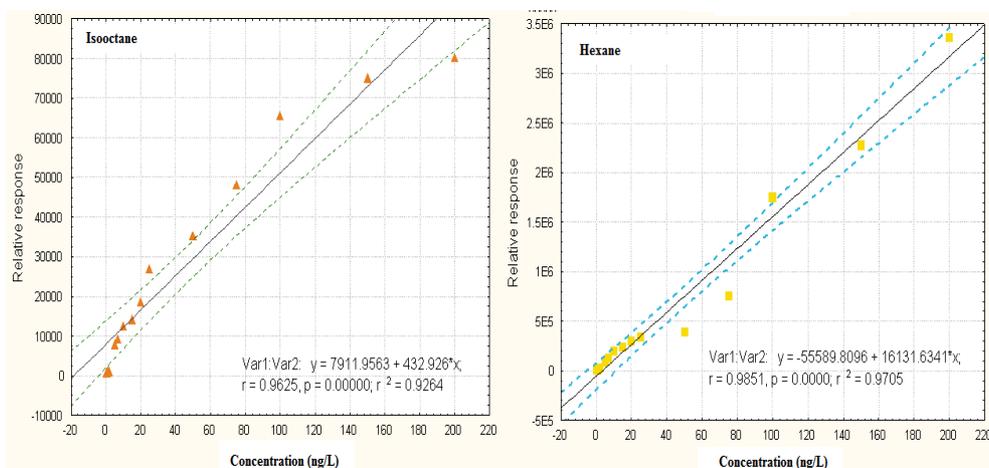


Fig. 2 – Solvent extraction efficiency in case of liquid-liquid extraction (LLE).

In several studies has been demonstrated that once with agitation it is lowered the time required for extraction time because the equilibrium between phases (water and headspace as well fiber coating) is more rapidly achieved. This resulted in increasing of extraction rate. In our study the water sample matrices was subjected to different stirring rate in order to achieve a higher response from the target organometallic compounds. The following stirring rates were tried on our water sample matrices: 0, 100, 250, 500, 750, 1 000, 1 200, 1 400, 1 800, 2 500 and 3 000 rpm, respectively. From these good response was obtained at 1 400 rpm was obtained, hence this was considered in the next analysis. But in most of SPME case just through sample stirring, the HS-SPME method performance can't be increased well, therefore the time appropriate for extraction is extremely important because through this is enhanced the equilibrium between the involved phases as headspace, water and fiber coating. In the next several experiments were done in order to choose the most convenient extraction time. Considering the antecedent studies it was supposed that an increasing extraction time foster achieving a better response from the target analytes. In this case times between range of 1–10 minutes proved good extraction efficiency, therefore 5 minutes was settled for extraction has proved to be quiet enough, therefore this considered for the next – see Fig. 3. As desorption time, 10 minutes was found to be optimal at 240 °C.

Throughout these optimization of sample preparation and extraction good performance were obtained on GC-qMS analysis. Method performance parameters as limit of detection, recovery and correlation coefficient values of all target organometallic compounds are presented in Table 1.

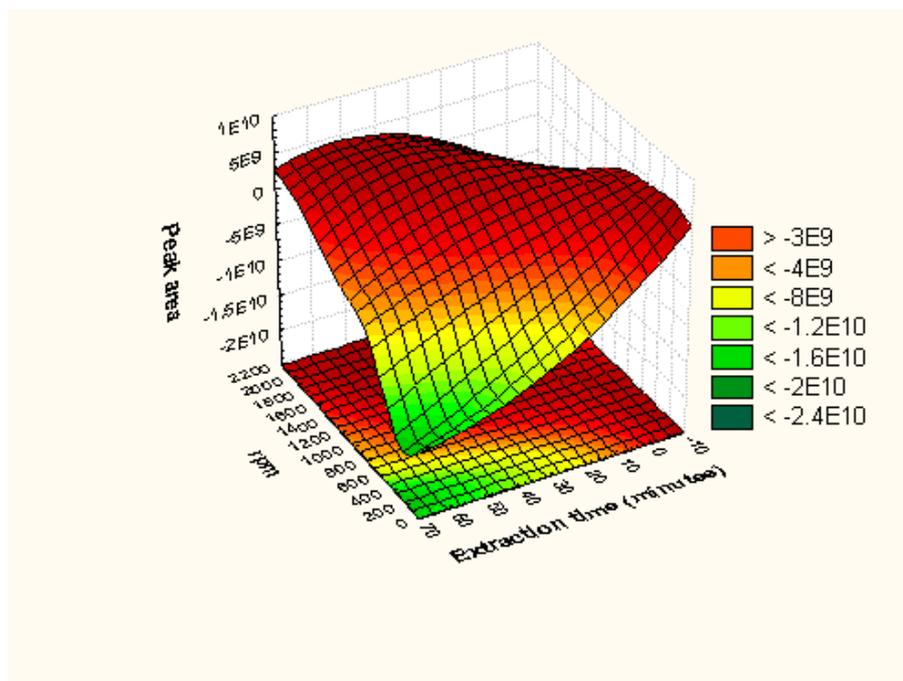


Fig. 3 – Solid phase microextraction (SPME) efficiency optimization through adjustment of extraction time and stirring rate.

Table 1

Data regarding method performance in case of organometallic compounds determination from water matrix

Compounds	Correlation coefficient	Recovery (%)	Limit of detection (ng·L ⁻¹)	R.S.D. (%)
<i>MBT</i>	0.9958	88	25	3.5
<i>DBT</i>	0.9985	105	12	2.8
<i>TBT</i>	0.9967	96	56	4.0
<i>TML</i>	0.9954	93	16	1.8
<i>TEL</i>	0.9942	101	20	3.2
<i>MeHg</i>	0.9944	116	18	3.0

4. CONCLUSIONS

The analytical feature of the HS-SPME-GC-MS method was evaluated. Optimization of this technique allowed attaining of lower limits of detection (12–56 ng·L⁻¹) without alteration of linearity (15 ng·L⁻¹–100 µg·L⁻¹, n = 9). Through this proposed method good linear regression (n ≥ 0.9950) and repeatability was obtained. Optimization of this method allowed the evidence of

compounds as organolead, organotin and organomercury in Somes River basin between ranges of 0.5–2.65 $\mu\text{g}\cdot\text{L}^{-1}$, 25–98 $\text{ng}\cdot\text{L}^{-1}$ and 22 $\text{ng}\cdot\text{L}^{-1}$ –0.9 $\mu\text{g}\cdot\text{L}^{-1}$, respectively.

REFERENCES

1. I. Ali, H.Y. Aboul-Enein, H. Y. Instrumental Methods in Metal Ion Speciation, in Chromatographic Science Series, 84–125, New York, John Wiley, USA, (2006).
2. D. Adelman, K.R. Hinga, M.E.Q. Pilson, M. E. Q. Environ. Sci. Technol. **24** 1027–1045, (1990).
3. E.J. Bulten, H.A. Heinema, Tin. In: Merian E, ed. Metals and their compounds in the environment. Weinheim, Germany: VCH, 1243–1259, (1991).
4. K. Gardfeldt, J. Munthe, D. Strömberg, O. Lindqvist, . Sci. Total Environ., **304** 127–136, (2003).
5. IARC (International Agency for Research on Cancer). Overall evaluations of carcinogenicity to humans: As evaluated in IARC Monographs volumes 1–82 (at total of 900 agents, mixtures and exposures). Lyon, France: International Agency for Research on Cancer. In: <http://www-cie.iarc.fr/monoeval/crthall.html>. (2005).
6. P.W. Looser, S. Bertschi, K. Fent, Appl. Organomet. Chem. **12** 601–611. (1998).
7. D.R. Parkinson, I. Bruheim, I. Christ, J. Pawliszyn, Journal of Chromatography A, **1025** 77–84 (2004).
8. R. Zufiurre, B. Pons, C.J. Nerin, Chromatogr A, **779** 299–306 (1997).