

Optical emission spectrometric determination of trace metals by solid phase microextraction of their volatile species and subsequent thermal desorption into a miniaturized helium plasma

Krzysztof Jankowski*

Department of Analytical Chemistry, Faculty of Chemistry, Warsaw University of Technology,
Noakowskiego 3, 00-664 Warszawa, Poland

ABSTRACT

A compact kHz rotating field plasma operated with helium as working gas at ambient atmosphere has been evaluated as a spectrochemical radiation source directly coupled with solid-phase microextraction (SPME) and subsequent thermal desorption (TD), and the suitability of the system for the determination of volatile metallic species has been studied by optical emission spectrometry (OES). Stable doughnut-shaped rotating field plasma with a central channel could be maintained within a wide range of operating conditions. Low power levels of 50-250 W and low He flow rates of 50-1500 mL min⁻¹ were used. A TD unit, consisting of a heated, glass-lined splitless-type GC injector, was connected directly with the dual-flow injector of the plasma approach to minimize the length of transfer line. This arrangement provides fast desorption and high sample introduction efficiency. The system can be combined with a miniaturized spectrometer with CCD detection, whereby avoiding space-angle limitations. The TD-plasma-OES system was used for the recording of time-resolved emission spectra for various analyte vapors at different working conditions. Both direct liquid immersion and headspace modes of SPME sampling can be employed for separation of compounds of interest. The compact

combination of SPME, thermal desorption, low cost helium miniplasma source and the miniature OES instrument led to a powerful and sensitive miniaturized system for trace metals analysis. For the selected measurement conditions, the detection limits for As, Se, Cr and Hg were at the low ppb level. The linearity ranges are up to 1000 ng mL⁻¹ and the precision is on the order of 3-7%.

KEYWORDS: optical emission spectrometry, low frequency plasma, solid phase microextraction, trace metal analysis

INTRODUCTION

Various compact analyzers based on spectroscopic techniques are increasingly used for routine environmental monitoring and product quality control. In the case of monitoring trace organic and organometallic pollutants, solid phase microextraction (SPME) may sometimes be used for the isolation and preconcentration of analytes. Next, thermal desorption (TD) coupled with gas or liquid chromatography is usually used as a separation technique [1-4]. However, the GC can sometimes be eliminated in these cases, and TD interface can also be used for the direct desorption of analytes into such element specific detectors as AAS, MIP-OES or ICP-MS. Although these lab-based instruments are highly sensitive and capable of multi-element detection, the instrument systems are too bulky to be employed cost-effectively in

*kj@ch.pw.edu.pl

the field study or screening analysis and exhibit some other technological limitations for real-time *in situ* monitoring of multiple elements. Thus, miniaturized instruments are extensively explored. Optical emission spectrometry (OES) is enormously versatile in applications in chemical analysis of gaseous microsamples and has been successfully downscaled including both excitation sources and OES detectors [5-7]. The atomic emission detector is particularly valuable for metals and has been used extensively for determination of environmentally relevant organometallic compounds [1-3, 8-11]. By using the detector in the selective mode at the wavelength selected for the element introduced, very high selectivity for the individual compound or group of element-containing analytes should be attainable. Numerous TD-GC-OES devices have been proposed for element speciation over recent years. However, the total concentration of a metal present in the sample in different chemical forms or various sum parameters are also good indicators of sample pollution, with regard to screening analysis.

TD is generally used with GC as a powerful and versatile sample introduction technique. However, it can also be used with alternative vapor-phase analytical options including direct optical emission or mass spectrometry [8, 12-13]. It is readily automated and serves to combine sampling and efficient introduction in one fully-automated procedure. In its simplest form, TD involves heating sample materials or sorbents in a flow of inert carrier gas, so that retained organic volatiles and semi-volatiles are vaporized/desorbed from the sample matrix/support and are transferred to the other section of an analytical instrument in the carrier gas stream. In general, key method parameters include temperature, carrier gas flow rate, desorption time and sorbent type selection.

Conventional off-line SPME sampling modes with subsequent TD provide a useful microextraction tool for complex samples and are extensively applied to monitoring thousands of volatile compounds in environmental samples and food products. It is also applicable for separation of various metal organic compounds [8, 11-19]. SPME is an equilibrium-based extraction technique, where only a small fraction of the analyte present in the sampled phase is separated

by the sorbent. Retained vapors are then desorbed and transferred with carrier gas. SPME allows separation of volatiles and semi-volatiles from samples and high concentration factors to be comfortably achieved. Other significant advantages are the following. Depending on the volatility of the compounds of interest, SPME usually facilitates effective elimination of sample interferences such as solvent or other matrix components prior to analysis. This allows analytes to be transferred with up to 100% efficiency into the analytical system with minimal interference. Moreover, in contrast to solvent extraction techniques, SPME is inherently safer with using microvolumes of toxic or odorous solvents. Finally, SPME fibers are automatically cleaned during the TD process that is convenient for multiple injections.

The main objective of the present work is to demonstrate a miniaturized SPME-TD-plasma-OES apparatus intended for the sampling and determination of volatile metallic species. In an attempt to address this issue, miniplasma operating at kHz frequency has been developed, due to its compact size, low power consumption, low gas flow rate, and high excitation efficiency, and combined with a miniaturized OES spectrometer with CCD detection. A few examples are presented that might serve to inspire thinking along similar lines for other applications.

MATERIALS AND METHODS

Apparatus

The major instrument components are a kHz-driven plasma device, a plasma power generator, a plasma electronic control module, a TD unit, a gas flow module, and a compact OES spectrometer (180-300 nm, resolution 0.04 nm).

A plasma source operating at ambient atmosphere has been developed by applying a synchronically rotating field with four phases operating at 6 kHz produced within 4 electrodes positioned in the plane around the axis. A TD-plasma interface consists of one heated quartz tube, being used for sample evaporation, and subsequent vapor transportation and injection to the plasma. This ensures the compactness of the device and heating of the transfer line, and also minimizes the length

of transfer line preventing the condensation of analyte and the interaction of analyte with the wall of the transfer line, particularly important for the analysis of very reactive species. Using an adopted quartz-lined splitless-type GC injector directly connected to the dual-flow injector permits the analyte thermally desorbed from the SPME fiber to be introduced with a make-up flow of helium directly into the plasma. A carrier gas line was introduced via a side arm of the TD unit to accommodate the gas flow needed for efficient transfer of analyte from the fiber to the plasma. Gaseous microsample introduction enables operation of the plasma at a relatively low power level of 50-250 W. The plasma gas is supplied through the outer tube of the dual-flow injector. This arrangement provides an extremely fast, high-throughput analysis of volatile metallic compounds. Fig. 1 shows details of this setup.

Emissions generated by the plasma were collected very close to the plasma using a 2 m long optical fiber connected to an OES spectrometer that was interfaced with a CCD detector. The emission recording systems were controlled by personal computer equipped with AvaSpec software. Operating parameters, such as the plasma gas flow rate, sample gas flow rate, plasma power, etc. are listed in Table 1.

Chemicals

All the chemicals were of analytical or higher grade. Standard solutions of As, Cr, Hg and Se for spectroscopy were obtained from Merck.

The derivatizing agents solutions were prepared as follows:

A 5% (m/v) aqueous solution of sodium borohydride (Sigma-Aldrich, CAS 16940-66-2) was prepared daily in a 0.1 M sodium hydroxide medium. The solution was used for generation of Hg vapor and arsenic hydride from 1-2 M HCl medium.

A 1% (m/v) solution of 4,5-dichloro-1,2-phenylenediamine (Sigma-Aldrich, CAS 5348-42-5) was prepared in a 0.1 M hydrochloric acid ethanol solution. The reagent was used for obtaining piäzselenol in aqueous solution.

A 25% (m/v) solution of 1,1,1- trifluoro-2,4-pentadione (Sigma-Aldrich, CAS 367-57-7) was prepared in methanol. The solution was used for obtaining chromium complex in buffered aqueous solution of pH 9.

Table 1. Operating parameters of the TD-plasma-OES device.

Frequency/ kHz	6.0
Incident Power/ W	50 - 250
Number of electrodes	4
Carrier gas flow rate/ mL min ⁻¹	50 - 500
Plasma gas flow rate/ mL min ⁻¹	0 - 1000
Wavelength range/ nm	180 - 300

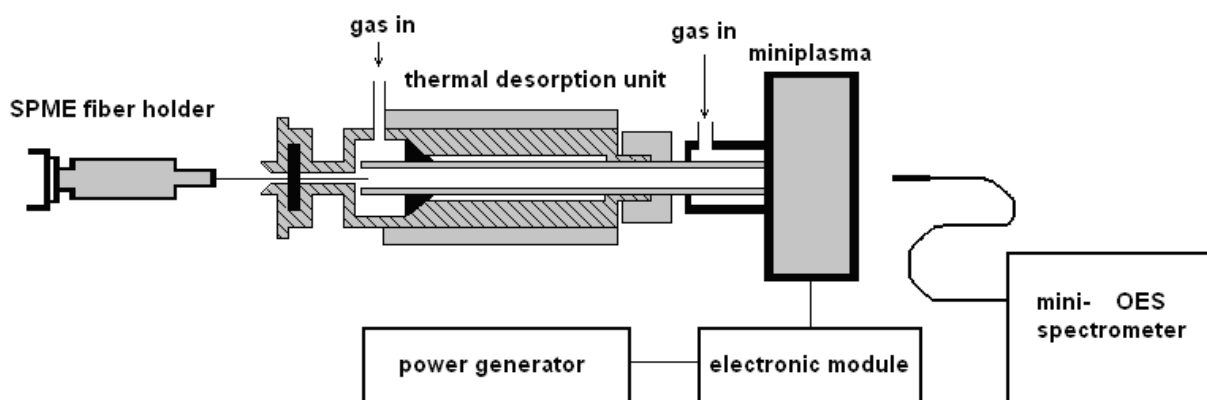


Fig. 1. Schematic diagram of the SPME-TD-plasma-OES instrument.

RESULTS AND DISCUSSION

Instrument operation and optimization

A plasma source was constructed based on the rotating field concept and the digitally controlled modulation of plasma heating, described elsewhere [20]. This new technology is highly flexible; thereby the number and the spatial arrangement of electrodes give more control over the shape of the plasma influencing, in particular, the geometry of central channel through which the sample is entrained. Waveforms of the plasma discharge current can have any shape, but with preserving digital energy efficiency achieved with a system of digital amplifiers.

In the presented device He plasma is generated in ambient atmosphere between 4 tungsten rod electrodes of 1 mm dia each, arranged in horizontal plane in a circle of 20 mm dia. When applying the central gas flow up to 0.5 L min⁻¹ doughnut shaped plasma is formed with a cold channel on axis. Thus, a 1.5 mm-long analytical channel is formed in the plasma where the sample in the form of vapor or gas is introduced, providing an efficient interaction between the sample and the plasma. The discharge becomes more diffuse with decreasing power. The length of the high temperature region in the plasma is much shorter than in common lab-based plasma sources resulting in shorter analyte residence time in the plasma. However, it is beneficial for obtaining a sharp transient signal. The contact between plasma and electrode is capacitive in nature, resulting in low background emission, and practically no etching of the electrodes is observed. Moreover, the plasma is self-igniting under experimental conditions examined in this study. The relatively strong emission from analytes in this low power, low gas flow, low frequency plasma indicated that the use of the miniplasma as an excitation source provides an advantage over lab-based high power plasma sources for OES measurements by a compactness of instrumentation.

The OES detector yields selective information about the sample components, and exhibits very useful characteristics, e.g. exceptionally high selectivity, large dynamic linear range, and excellent limits of detection. Moreover, the CCD detector can

be considered as a simultaneous multi-element-selective detector, because all the elements present in the sample can, in principle, be detected.

Fundamental to the SPME-TD-plasma-OES system is the development of an effective desorption-sample introduction module. The TD interface between the SPME and plasma-OES serves a dual function: to liberate the analyte from the polymer phase of the SPME and to transfer it to the detector. Under optimized conditions, desorption must be rapid and the transfer highly efficient.

The stability of plasma was examined prior to OES measurements. Stable doughnut-shaped rotating plasma was obtained at an operating plasma power ranging from 50 to 250 W and a helium gas flow rate in between 100 mL min⁻¹ and 1500 mL min⁻¹. Comparatively, at lower powers (< 50 W), plasma became slightly jittery; the emission intensities were highly fluctuating, imparting high noise to the signal. The most significant influence of the gas flow rate was on the shape of the plasma plume. Stable doughnut-shaped plasma was obtained at total helium gas flow rate higher than 400 mL min⁻¹. After a series of optimization procedures, the most stable emission signal was achieved when the plasma operated at 150 ± 30 W and a gas flow rate of 500 ± 100 mL min⁻¹, depending on each of individual sample.

The emission intensity of the Hg 253.6 nm line as a function of power (50-250 W) as well as of the flow rate of the working gas (50-1000 mL min⁻¹) was evaluated. It was found that an increase of power over 120 W did not lead to a large increase of the intensity for Hg line.

Under these conditions (120 W) different He flow rates were tested, achieving the highest Hg emission intensity when using a helium flow rate of 150 mL min⁻¹. Equal, or even lower, signals were obtained when rates higher than 150 mL min⁻¹ were used. The plasma gas flow rate was kept constant during all optimization experiments being of 400 mL min⁻¹.

SPME sampling procedure

Trace metals are usually present in samples of environmental origin as non-volatile species.

Thus, a derivatization procedure is necessary before SPME sampling to give TD-active derivatives with advantageous detection properties. Both inorganic and metal organic compounds can be considered to be used for OES detection. They include atomic vapors, volatile hydrides, chlorides, acetylacetonates and others. The overall selectivity of the SPME-TD-plasma-OES method depends on the selectivity of derivatization reaction used and the selectivity of OES detection. Both direct liquid immersion (DI) and headspace (HS) modes of SPME sampling can be employed for preconcentration of compounds of interest. Traditional equilibrium HS sampling is fundamentally static method which relies on target compounds partitioning reproducibly between the sample and the HS phase, and between the HS phase and the SPME fiber coating under selected conditions, so that analyte amounts adsorbed on the fiber are representative of analyte concentration in the sample. This double equilibration process may account for the longer exposure time required with the SPME fiber lasting even 1 hour. HS sampling is not suitable for less volatile organometallic compounds, since a long equilibration time is required to ensure the adsorption efficiency. Generally, HS sampling is more specific and can be used to selectively separate the analyte from complex matrices. DI technique is more effective being the one equilibration process and typically offers shorter exposure times. However, it is less selective as such and therefore highly selective derivatization procedures are

required. In practice, these limitations require a careful method design and a detailed study of potential competitive interferences in real samples.

In general, the sampling procedure is as follows: a 10 mL volume of sample solution is placed in a septum-sealed 20 mL glass vial. Next, a derivatization agent is added and the sample is allowed to stand in a predetermined reaction time and temperature to produce a suitable volatile species. The SPME fiber was then inserted into the HS or immersed in the sample solution for a predetermined sampling time and temperature, depending on the experiment. The fiber was then withdrawn and transferred to the TD unit for TD-plasma-OES measurement.

In order to optimize the SPME method, metal-containing solutions were analyzed using different exposure times, exposure temperatures and concentrations of matrix components including derivatizing agent and mineral acid. For HS sampling of inorganic compounds of Hg and As, reasonably short exposure times were necessary, ranging from 0.5 to 2 min. For DI sampling of organic complexes of Cr and Se, equilibration between the solution and the exposed fiber was significantly slower achieving 30 min if only the sample solution was heated up to 40-75°C. The optimum conditions for As, Cr, Hg and Se determination are summarized in Table 2.

Desorption procedure

Since SPME is generally a solvent free sampling technique, the entire volume of the desorbed

Table 2. Operating parameters of the SPME separation.

Element	Derivatization	SPME fiber	Exposure time	Exposure temperature	Desorption temperature
As	0.05 % NaBH ₄ ; 2 M HCl; 5 min., 25°C	Carboxen/ PDMS	2 min.	25°C	150°C
Hg	0.04 % NaBH ₄ ; 1 M HCl; 5 min., 25°C	Carboxen/ PDMS	0.5 min.	25°C	150°C
Cr	0.06 % trifluoro-pentadione; pH 9; 60 min., 75°C	DVB/Carboxen/ PDMS	30 min.	75°C	250°C
Se	0.04% dichloro- phenylenediamine 10 min; 40°C	PDMS	30 min.	40°C	270°C

analyte can be introduced into the plasma without any disturbance. TD of volatile analytes was achieved by insertion of the SPME fiber through the septum of the TD injector, where it was exposed and withdrawn after 1 min. Fast desorption of the analyte is promoted by the use of narrow one-piece injector liner specifically designed for this TD-plasma device. Because of the small volume of the SPME extraction phase, desorption can often be quickly achieved and the analyte can be introduced in a very narrow zone, thereby significantly improving the measurement sensitivity. Slow desorption of the analyte from the fiber can cause broadening of the transient peak, in addition to reduced analyte sensitivity as a result of dilution. Higher desorption temperatures resulted in improved transient peak shapes having less tailing, but at the expense of fiber lifetime. Selection of optimum temperatures is usually straightforward, taking into account both the volatility and thermal stability of the compounds of interest and the temperature limits of the fiber coating concerned.

Typical flow rates used in TD are in the order of 20–300 mL min⁻¹ being highly compatible with plasma operating conditions. Increasing flow can be sometimes a very useful alternative to raising temperatures - for example, when analyzing reactive compounds i.e. hydrides.

For volatile compounds such as Hg vapor or AsH₃, the desorption temperature applied (150°C) results in rapid release (3–5 s transient peak width) of the analyte (see Fig. 2a). For semi-volatile piarselenol and Cr(TFA)₃ complexes, the TD unit temperature was set to the maximum value suggested by the supplier of the SPME fiber (250°C) to obtain flash desorption and the fiber was held for 1 min inside the injector for completing the desorption.

Data collection was arbitrarily started a few seconds prior to the insertion of the fiber to permit establishment of a stable baseline. A significant advantage of both the sample introduction method and He miniplasma is a low associated background. An applied 1 min desorption time resulted in complete clean-up for samples in the ng mL⁻¹ concentration range. The use of a pre-drilled septum is highly recommended to avoid the SPME needle damage.

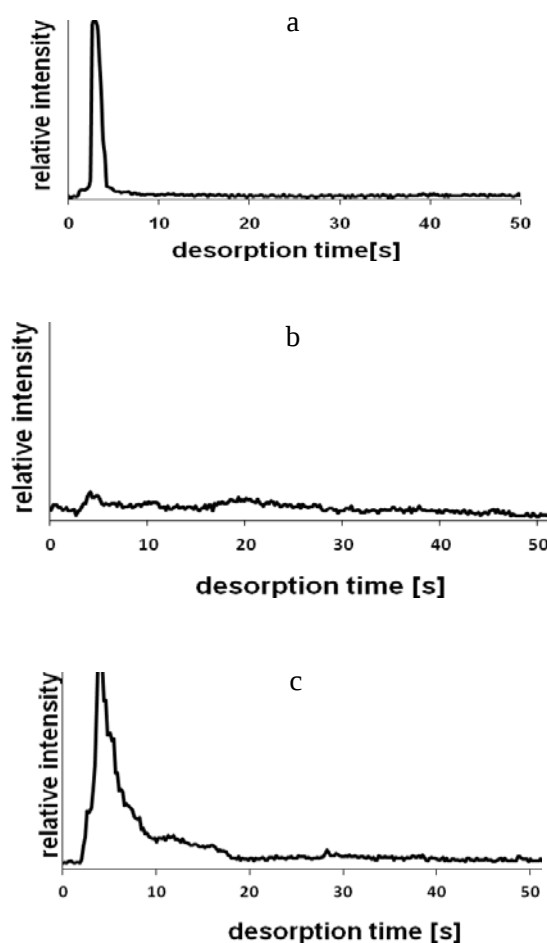


Fig. 2. Transient signals arising from desorption of (a) Hg vapor at 253.6 nm; (b) sample blank at 283.6 nm; (c) Cr(TFA)₃ registered for Cr at 283.6 nm.

Analytical performance

Two sampling modes for the SPME can be alternatively applied, (1) DI of the fiber into the sample solution and (2) HS extraction. The suitability of a miniaturized compact TD-plasma-OES device for the determination of Hg by batch cold vapor generation, using NaBH₄ as the reducing agent, HS-SPME sampling and OES detection using a small CCD spectrometer was evaluated. The SPME fiber with Carboxen/PDMS coating was used. Under similar chemical conditions arsenic can be determined after conversion into AsH₃.

A limit of detection (LOD) of 0.4 ng mL⁻¹ for mercury vapor can be achieved for the measurement of this analyte in aqueous solution.

The signal level depends strongly on the carrier gas flow rate and to a smaller extent on the residence time of the sample in the plasma, as it has been shown that the He miniplasma offers the lower LOD for Hg compared with the microwave induced plasma ($0.5\text{--}0.9\text{ ng mL}^{-1}$) [5, 11, 17]. However, the LODs by OES are slightly higher compared with ICPMS and AAS [16, 21]. The linearity range is up to 1000 ng mL^{-1} and the precision is on the order of 5%, as expected for SPME performance. With the optimized HS SPME-TD-plasma-OES method a determination of Hg in spiked natural waters at concentration levels up to $100\text{ }\mu\text{g L}^{-1}$ could be performed.

When the 3σ criterion is used a LOD of 0.1 ng mL^{-1} for arsenic at 228.8 nm was found with OES using the HS sampling and the TD-plasma system. The proposed method allowed determination of total arsenic in various samples including drinking water and beverages with a good linear response range $1\text{--}50\text{ }\mu\text{g L}^{-1}$.

Direct liquid immersion of piarselenol complex with PDMS coated fiber was studied, including the effect of time and temperature of complex formation and sampling on the extraction efficiency. DI sampling provided good sensitivity that was linear over two orders of magnitude whereas precision showed typically 7%. Any inhomogeneity of the SPME fiber coating may result in a significant difference in its extraction characteristics. Concerning the quality of the results with respect to fiber-to-fiber performance, this effect could be more pronounced in the case of HS rather than DI sampling. However, in this study, this general rule does not correspond with the precision data suggesting that desorption process is responsible on the precision of the measurement.

The LOD for DI $\text{Cr}(\text{TFA})_3$ sampling with PDMS coated fiber was 2 ng mL^{-1} being similar to those by different TD and GC methodologies [10, 18–20, 22]. The reproducibility of repetitive DI sampling measurements was again 7% RSD. The methodology was successfully applied for trace Cr determination in cereals.

The sharp transient signal obtained for Hg 253.6 nm enables the use of the peak height for the calibration instead of the peak area which

simplifies the calibration procedure. The shape of the peak indicates that desorption of Hg vapor from the Carboxen/PDMS coating is relatively fast. Typical transient emission signals recorded for Cr 283.6 nm are shown in Fig. 2 in the case of a blank solution (2b) and of 50 ng mL^{-1} solution (2c). Interestingly, with the present system an increase in the spectral background was always observed during the desorption step. An increase in the background intensity can indeed be expected since spectroscopic observation of He plasma has shown the existence of the intensive lines of OH close to the Cr line.

CONCLUSION

Direct coupling of SPME with TD- miniplasma-OES provides a cost-effective miniaturized approach for both the sampling and sample introduction of volatile metallic species into an atomic spectroscopic detector. A stable 6 kHz frequency miniplasma operated at ambient pressure with a power of $50\text{--}250\text{ W}$ and at a gas flow of $0.1\text{--}0.6\text{ L min}^{-1}$ of helium in a multi-electrode rotating field approach forms a 1.5 mm diameter plasma channel for introduction of analytes. The device is shown to be useful for the excitation of atomic (and molecular) species and for the sensitive OES determination of metals down to a few ng mL^{-1} -level, as shown for the case of As, Cr, Hg and Se. The development of the planar plasma based on the multi-phase rotating field leads to the elimination of the plasma fringe resulting in a reduction of the background level, thereby significantly improving sensitivity, and most applications can be performed using axially viewed plasma without any serious degradation of OES analytical performance.

It is obvious that selective separation using SPME in combination with selective and sensitive OES detection has several unique properties that can be used very profitably in complex analytical tasks. The compact design of the TD-mini-plasma-OES device provides significant reduction of the length of the transfer line, particularly important for the analysis of very reactive species including hydrides as well as for obtaining well-shaped transient peaks. For complex samples containing volatile components, HS extraction is recommended.

DI extractions, on the other hand, are less-selective and are therefore limited when more than one extractable compound is present. Thus, the use of highly selective derivatizing agent is required. The results of this study testifies that it will be possible to obtain a highly sensitive and successfully miniaturized total analysis system for the determination of traces of metals with the SPME-TD-mini-plasma approach by using a miniaturized OES spectrometer. Furthermore, this instrument has the advantage of being robust and easy to handle and allows fast analysis.

ACKNOWLEDGEMENTS

This work was financially supported by the Warsaw University of Technology.

REFERENCES

1. Twiehaus, T., Evers, S., Buscher, W. and Cammann, K. 2001, *Fresenius J. Anal. Chem.*, 371, 614.
2. Wasik, A., Lobinski, R. and Namieśnik, J. 2001, *Instrum. Sci. Technol.*, 29, 393.
3. Rosenkranz, B., Breer, C. B., Buscher, W., Bettmer, J. and Cammann, K. 1997, *J. Anal. At. Spectrom.*, 12, 993.
4. Gil-Moltó, J., Varea, M., Galindo, N. and Crespo, J. 2009, *J. Chromatogr. A*, 1216, 1285.
5. Jiménez Zapata, I., Pohl, P., Bings, N. H. and Broekaert, J. A. C. 2007, *Anal. Bioanal. Chem.*, 388, 1615.
6. Jankowski, K., Ramsza, A. P. and Reszke, E. 2011, *Spectrochim. Acta, Part B*, 66, 500.
7. Jankowski, K., Ramsza, A. P., Reszke, E. and Strzelec M. 2010, *J. Anal. At. Spectrom.*, 25, 44.
8. Tyburska, A., Jankowski, K. and Rodzik, A. 2011, *Spectrochim. Acta, Part B*, 66, 517.
9. Khuhawar, Y., Sarafraz Yazdi, A. and Uden, P. C. 2002, *Chromatographia*, 56, 729.
10. Black, M. S. and Browner, R. F. 1981, *Anal. Chem.*, 53, 249.
11. Rodil, R., Carro, A. M., Lorenzo, R. A., Abuin, M. and Cela, R. 2002, *J. Chromatogr. A*, 963, 313.
12. Mester, Z., Sturgeon, R. E. and Lam, J. W. 2000, *J. Anal. At. Spectrom.*, 15, 1461.
13. Guo, X., Mester, Z. and Sturgeon, R. E. 2002, *Anal. Bioanal. Chem.*, 373, 849.
14. Kaur, V., Malik, A. K. and Verma, N. 2006, *J. Sep. Sci.*, 29, 333.
15. Mester, Z. and Sturgeon, R. E. 2002, *Environ. Sci. Technol.*, 36, 1198.
16. Mester, Z., Lam, J., Sturgeon, R. E. and Pawliszyn, J. 2000, *J. Anal. At. Spectrom.*, 15, 837.
17. Snell, J. P., Frech W. and Thomassen, Y. 1996, *Analyst*, 121, 1055.
18. Ding, T. H., Lin, H. H. and Whang, C. W. 2005, *J. Chromatogr. A*, 1062, 49.
19. Abranko, L., Yang, L., Sturgeon, R. E., Fodor, P. and Mester, Z. 2004, *J. Anal. At. Spectrom.*, 19, 1098.
20. Jankowski, K., Ramsza, A. P., Reszke, E. and Tyburska, A. 2012, *J. Anal. At. Spectrom.*, 27, 1287.
21. Murphy, J., Jones, P. and Hill, S. J. 1996, *Spectrochim. Acta, Part B*, 51, 1867.
22. Bermejo-Barrera, P., Barciela-Alonso, M. C., Perez-Fernandez, B. and Bermejo-Barrera, A. 2003, *Spectrochim. Acta, Part B*, 58, 167.