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Electrothermal atomic absorption spectrometric determination of arsenic in essential lavender and rose oils

Irina B. Karadjova[a], Leonardo Lampugnani[b,*], Dimiter L. Tsalev[a]

[a] *Faculty of Chemistry, University of Sofia, 1 James Bourchier Blvd., Sofia 1164, Bulgaria*
[b] *C.N.R. Istituto per i processi chimico-fisici, Area della Ricerca di Pisa, Via Moruzzi 1, 56124 Pisa, Italy*

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Abstract

Analytical procedures for electrothermal atomic absorption spectrometric (ETAAS) determination of arsenic in essential oils from lavender (*Lavendula angustifolia*) and rose (*Rosa damascena*) are described. For direct ETAAS analysis, oil samples are diluted with ethanol or *i*-propanol for lavender and rose oil, respectively. Leveling off responses of four different arsenic species (arsenite, arsenate, monomethylarsonate and dimethylarsinate) is achieved by using a composite chemical modifier: L-cysteine (0.05 g l^{-1}) in combination with palladium (2.5 μg) and citric acid (100 μg). Transverse-heated graphite atomizer (THGA) with longitudinal Zeeman-effect background correction and 'end-capped' graphite tubes with integrated pyrolytic graphite platforms, pre-treated with Zr–Ir for permanent modification are employed as most appropriate atomizer. Calibration with solvent-matched standard solutions of As(III) is used for four- and five-fold diluted samples of lavender and rose oil, respectively. Lower dilution factors required standard addition calibration by using aqueous (for lavender oil) or *i*-propanol (for rose oil) solutions of As(III). The limits of detection (LOD) for the whole analytical procedure are 4.4 and 4.7 ng g^{-1} As in levender and rose oil, respectively. The relative standard deviation (R.S.D.) for As at 6–30 ng g^{-1} levels is between 8 and 17% for both oils. As an alternative, procedure based on low temperature plasma ashing in oxygen with ETAAS, providing LODs of 2.5 and 2.7 ng g^{-1} As in levender and rose oil, respectively, and R.S.D. within 8–12% for both oils has been elaborated. Results obtained by both procedures are in good agreement.
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Keywords: Essential oils; Lavender oil; Rose oil; Arsenic determination; Electrothermal atomic absorption spectrometry; Chemical modification; L-Cysteine

1. Introduction

Owing to its toxic, cumulative and carcinogenic effects, arsenic is a popular yet very difficult analyte element at ng g^{-1} levels in environmental, nutritional, clinical, pharmaceutical and other fields [1–3]. Analysis of samples with high oil/fat contents represents a serious analytical challenge in analysis of edible and mineral oils [4–10] because of difficulties in complete decomposition of these particular matrices by dry ashing or wet digestion without entailing volatilization losses, intolerable blanks, prolonged pretreatments and other negative effects. Upon digestion, several instrumental techniques provide LODs in the sub-ng g^{-1} As range: atomic absorption spectrometry (AAS) [4], inductively coupled plasma atomic emission spectrometry (ICP-AES) [5] and atomic fluorescence spectrometry (AFS) [7], following hydride generation (HG) of AsH_3 from acidic sample digests [3]; the decomposition of the organic/oil matter is performed by microwave digestion [7], oxygen bomb combustion [4] or by dry ashing in the presence of ethanolic $Mg(NO_3)_2$ ashing aid [5]. Electrothermal AAS is particularly attractive technique [6,8–11] offering instrumental LODs down to 1–2 ng g^{-1} (10–20 pg absolute); microlitre volumes of oily samples could be directly injected in the graphite atomizer after dilution [10], alkaline solubilization [6,8] or micro emulsification [9]. A more sensitive technique, the inductively coupled plasma mass spectrometry has found scarce applications to samples

* Corresponding author. Tel.: +39 050 3152294; fax: +39 050 3152555.
E-mail address: lampugnani@ipcf.cnr.it (L. Lampugnani).

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of crude oils and fractions [12,13] but arsenic has not been addressed in those studies.

High quality essential oils are produced by steam distillation and volatile elements such as As can be transferred to the final product. Migration processes of trace elements from plants to the final product call for evaluation. Although careful investigation of the whole technological scheme is required, the availability of accurate, precise and reliable procedures for the determination of volatile toxic elements in micro samples of the final product is indispensable. According to our knowledge there are no papers dealing with arsenic determination in essential oils. The aim of the present study is to elaborate a simple and robust method for As determination in two important types of essential oils produced from lavender (*Lavendula angustifolia*) and rose (*Rosa damascena*). Analytical procedure should be based on direct injection of diluted samples and performing in situ chemical treatments: (i) isoformation and efficient thermal stabilization of volatile arsenic species eventually present in this oil matrix; (ii) efficient elimination of the organic/oil matrix during the pyrolysis stage; (iii) using of suitable organic solvents with appropriate physical properties, mutual solubility with oils, aqueous standards and aqueous solutions of chemical modifiers, stability on storage as well as compatibility with autosampler conduits; (iv) optimisation of instrumental parameters for best sensitivity and minimized matrix effects; and (v) versatile calibration by means of aqueous standard solutions.

2. Experimental

2.1. Instrumentation

The measurements were carried out with Perkin-Elmer Model 4100 ZL atomic absorption spectrometer equipped with a transverse heated graphite atomizer (THGA), longitudinal Zeeman effect background corrector and an AS-71 autosampler. 'End-capped' THGA graphite tubes with integrated platforms (Part no. B300-0653) were either used as purchased or otherwise pre-treated with a carbide forming element (referred as Ir–Zr treated platform). The experimental procedure for treatment of integrated platforms and deposition of Ir (8 μg) on zirconium (250 μg) as permanent chemical modifier has been described elsewhere [14,15]. Instrumental parameters for AAS measurements are presented in Table 1. The measurements were in peak area mode (integrated absorbance, A_{int}). Sample aliquots of 10 and 5 μl modifier injections were performed successively. Washing solution for autosampler capillary between samples and modifier injections was 0.2% (v/v) HNO_3; thus, no problems with clogging due to the oil matrix were observed. Precautions to minimize tube memory effects and cross-contamination have been taken: in all cases modifiers were applied from the lowest to higher concentration levels and individual graphite tubes were used for each modifier. The mixture of Pd and ascorbic acid is unstable, hence these modifier components are introduced into the graphite tube by separate injections.

Pressurized microwave decomposition was performed in Model 4781 PARR PTFE bombs, 23 ml (PARR Instrument Company, Illinois, USA), rated to be safely used up to a temperature of 250 °C and a pressure of 1200 psig, fitted with quartz insert vessels in a Supratronic750 microwave oven rated for a maximum power of 850 W with turntable for homogeneous irradiation and programmable timer (MIELE).

Dry ashing of essential oils was carried out with Plasma System Low Temperature Asher (Branson model 1005-248AN).

2.2. Reagents

Stock standard solutions used for arsenic measurements were: 1000 μg ml^{-1} As(III) (atomic absorption spectroscopy standard solution, 11082, Fluka); 1000 μg ml^{-1} As(V), Titrisol standard, Merck, 9989; organoarsenicals were prepared by dissolving sodium methylarsonate (MMA), $CH_3AsO(ONa)_2{\cdot}6H_2O$ (Cod. 371205, Carlo Erba); sodium cacodylate (DMA), $C_2H_6O_2AsNa{\cdot}3H_2O$ (Cod. 367455, Carlo Erba). Ethanol absolute (Cod. 414607, Analyticals, Erba) and isopropyl alcohol (*i*-propanol), (Cod. 412712, for HPLC, Erba) were used for sample dilution. Solutions of carbide-forming chemical modifiers (1000 μg ml^{-1}) were prepared from 0.2535 g of zirconyl nitrate, $ZrO(NO_3)_2{\cdot}nH_2O$ (Cod. 495265, Analyticals, Erba), in 100 ml of 0.2% (v/v) HNO_3. Stock standard solution of palladium (Sigma, Lot 301255A) was 1005 μg ml^{-1} in 5% HCl and stock standard solution of iridium (Lot 2-1315, Alfa Johnson Mathey) was 1000 μg ml^{-1} in 20% HCl. The water used in all operations was prepared by means of a Milli-Q system (Millipore).

Solutions of other reagents were prepared from: L(+)-ascorbic acid (No. 1018, Baker Analyzed Reagent; citric acid (Pure, Carlo Erba).

Table 1
The optimized THGA (transverse-heated graphite atomizer) temperature program for direct ETAAS determination of As

Step no.	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow (ml min^{-1})	Read
1. Drying	80 (var. 60–80)[a]	20 (var. 20–40)[a]	10 (var. 20–40)[a]	250	–
2. Drying	130 (var. 80–400)	10 (var. 10–30)	10 (var. 10–30)	250	–
3. Pyrolysis	1400 (var. 400–1500)	20 (var. 20–30)	30 (var. 20–50)	250	–
4. Atomization	2300 (var. 2100–2500)	0	5	0	Yes
5. Clean	2350 (2550)[a]	1	2	250	–

[a] Range of parameters varied during optimisation studies given in parentheses.

2.3. Sample preparation

2.3.1. Direct ETAAS measurement

Essential oils are expensive, hence minute amounts are used in sample preparation procedures. Sample dilution is performed directly in an autosampler cup, placed on analytical balance pan, by dispensing appropriate amount of essential oil and organic solvent (ethanol or *i*-propanol), so as to obtain 1 + 2, 1 + 3 or 1 + 4 ($m\,m^{-1}$) dilution. Spiked samples were prepared by adding appropriate volumes (10–30 μl) of aqueous (for lavender oil) or *i*-propanol (for rose oil) standard solution of each arsenic species (500 ng ml^{-1} As). Cups were then sealed with Parafilm and shaken to obtain a homogeneous solution; diluted samples have proved stable for at least 1 week at room temperature. Cups were open before measurements in order to avoid uncontrolled evaporation of organic solvents.

2.3.2. Pressurized wet digestion in a microwave oven

Essential oil sample, ca. 0.2 g, was placed in a small quartz vial, 2 ml of nitric acid and 1 ml of H_2O_2 (30%) were added and the quartz vials were inserted in PTFE vessels, closed tightly with PTFE cups, and placed in a microwave oven for decomposition. Samples were heated following the temperature program: 150 W for 5 min; 0 W for 3 min; 300 W for 10 min; 0 W for 3 min; 450 W for 10 min; 0 W for 3 min and 800 W for 10 min. After cooling, the autoclaves were opened and quartz vials were heated on a hot plate until solutions slowly evaporated to near dryness. Several drops of deionized water were added and contents were quantitatively transferred to a 1-ml calibrated test tube by means of a micropipette, and diluted to the mark with deionized water.

2.3.3. Low temperature plasma ashing

Essential oil sample, ca. 0.3 g, is placed in small quartz vial and inserted in the ashing chamber. Ashing is performed according to the manual instructions. The flow rate of O_2 is adjusted so as to provide pressure within 2–3 mbar in the ashing chamber. After complete ashing (1 h), vial is taken out, 0.1 ml of HNO_3 (1:1) and 0.2 ml of deionized water are added with gentle heating on a hot plate. Digests are quantitatively transferred by micropipette to an autosampler cup for ETAAS measurements.

3. Results and discussion

Whereas a large variety of organic solvents is available for essential oil dilution prior to ETAAS measurements, preference has been given in this work to those solvents, which exhibit appropriate mutual solubility with both organic samples and aqueous standard solutions, as well as adequate (low) viscosity, (moderate) surface tension, (moderate) volatility, low toxicity and compatibility with autosampler conduits, without resorting to solvent-resistant autosampler parts. The goal was to obtain homogeneous, stable solutions of oils in the solvent, which permits additions of aqueous standards for calibration and aqueous solutions of chemical modifiers. In this way the autosampler could be used without changing the rinsing solution and without problems of clogging. Ethanol and *i*-propanol have been examined more thoroughly and proved the solvents-of-choice, the lavender oil being soluble in both these solvents at any ratio, while the rose oil is soluble only in *i*-propanol and diluted standard solutions should also be prepared in *i*-propanol for compatibility.

Various arsenic species may exhibit different behaviour in the graphite atomizer during thermal pretreatment and atomization, resulting in pre-atomization losses and species-dependent response. Therefore, oil samples spiked with four different arsenic species, known to be present in biological and environmental samples: arsenite, arsenate, MMA and DMA, were examined. The approach of 'composite chemical modifier' [16] containing an isoformer of various arsenic species plus efficient thermal stabilizer during high-temperature pyrolysis has been applied. Permanently-modified atomization surfaces have also been evaluated owing to their potential in analyses of organic extracts, solvents and samples containing volatile organoelement species [17,18].

3.1. Behaviour of arsenic species diluted in ethanol or *i*-propanol in the presence of L-cysteine

L-Cysteine is widely known as a pre-reductant and complexing agent in hydride generation AAS [3,19,20]; the products of reaction of aresenic species As(III), As(V), MMA and DMA with L-cysteine are supposedly thiolate complexes such as $As(Cys)_3$, $As(Cys)_3$, $As(CH_3)(Cys)_2$ and $As(CH_3)_2(Cys)$, respectively [20]. It could be expected that some degree of isoformation will be involved and their thermal behaviour during pyrolysis/atomization and sensitivity of ETAAS measurements will be levelled off. The thermal behaviour of all four arsenic species was studied in the presence of L-cysteine (0.05, 0.1 and 0.2 g l^{-1}) and several different modifiers by plotting pyrolysis and atomization curves for As species in ethanol and *i*-propanol solutions. The modifiers examined were Pd alone (2.5, 5 and 10 μg); Pd without and with reductant (2.5 or 5 μg Pd with 100 μg ascorbic acid); Pd with citric acid (2.5 or 5 μg Pd with 100 μg citric acid); and Ir (0.2 and 0.4 μg). Palladium and Ir are typical representatives of noble metal modifiers, taking into account literature data on their efficiency as thermal stabilizers and potential isoformers of arsenic species in aqueous solutions [16,21]. Rhodium and Rh plus citric acid [22] have also been tried, but proved worse isoformers than Pd and Ir, even in the presence of L-cysteine. Modifiers such as Ni or Cu, which efficiency could be similar to that of Pd [23,24] were ruled out in order to avoid contamination of graphite atomizer with these frequently determined elements. 'End-capped' graphite tubes with integrated platforms (as sold) as well as

graphite tubes with permanently modified Ir–Zr platforms [17,18] were used. Vaporization temperatures (T_{vap}), optimal atomization temperature (T_{at}) and characteristic masses (m_o) for the most efficient combinations are summarized in Table 2. Results obtained with ethanol or *i*-propanol solvents do not differ significantly, therefore, data for *i*-propanol diluent only are shown in Table 2. Both permanent Ir–Zr coating and reduced Pd modifier fail in thermal stabilization of arsenic species at high L-cysteine levels in sample solutions 0.1 or 0.2 g l^{-1}. It could be assumed that thiolate complexes of all arsenic species decompose at relatively low pyrolysis temperatures to arsenic sulfides with boiling points in the range of 500–700 °C, hence analyte losses are entailed in the presence of inappropriate modifier such as pre-reduced palladium or Ir–Zr treated platform only. It has been reported that $Pd(NO_3)_2$ is more suitable than other modifiers as an isoformer for arsenic determination in aqueous solutions but not in methanolic medium [25], and this proves to be valid also for ethanol or *i*-propanol solvents in the absence of L-cysteine. Latva et al. [26] found that with $Pd(NO_3)_2$ modifier even in aqueous solutions the atomization signal of these four arsenic species differ significantly and their accurate determination would require a separate calibration graphs for each species. Our data compiled in Table 2 demonstrate efficient thermal stabilization of all four arsenic species in the presence of 0.05 g l^{-1} of L-cysteine and Pd with ascorbic acid in 'end-capped' graphite tubes up to 1400 °C. However asymmetrical absorbance–time profiles with lower absorbance values were obtained for all arsenic species with this modifier using Ir–Zr treated platforms. Therefore, Ir–Zr treated tubes are preferred in the presence of L-cysteine only with Pd plus citric acid or with Ir modifier application, as summarized in Table 2. In this case absorbance-time profiles for different arsenic species are very similar in shape and appearance times, specific for each of these modifiers. Vaporization temperatures are in the range of 1300–1400 °C and optimal atomization temperature are confined to 2200–2300 °C.

3.2. Behaviour of arsenic species in the presence of lavender or rose oil matrix dissolved in ethanol or *i*-propanol

The aim has been achieving as complete as possible removal of oil matrix without losses of arsenic species. All attempts to use nitric acid in the sample solution, preparing emulsions from oils in the presence of surfactants or to use combination of nitric acid and hydrogen peroxide added as second modifier [23] and thus to assist in situ matrix decomposition were unsuccessful. Lower AAS signals with impaired peak shapes were obtained, and sample sputtering due to violent dry/ash sequence was observed, even with prolonged ramp heating times. Pyrolysis–atomization curves for all arsenic species were plotted in the presence of spiked lavender oil sample dissolved in ethanol or *i*-propanol or spiked rose oil sample dissolved in *i*-propanol, in the presence of the most efficient combination of modifiers and 0.05 g l^{-1} L-cysteine. These plots show similar behaviour for all As species in the presence of oil matrices and L-cysteine, therefore, only typical examples for DMA are depicted in Fig. 1. It is accepted that behaviour of modifier is a consequence of the interaction between the graphite support, modifier and analyte [23], but matrix could change dramatically this behaviour, as shown in Fig. 1. Surprisingly, worst results were obtained by using combination of Pd and ascorbic acid with 'end-capped' graphite tubes as atomizers; moreover, it was practically impossible to measure arsenic in the presence of Pd and ascorbic acid if Ir–Zr treated platforms are used as atomizers. The lower values of absorbance signals for all arsenic species, the shape of the absorbance–time profiles (noisy and wide peaks) and high background absorption observed could be explained by efficient thermal stabilization of some matrix components in the presence of this modifier, which disturbed atomization of arsenic species. Almost the same was observed with Ir modifier: lower arsenic signals and deteriorated peak shapes.

Table 2
Vaporization temperatures (T_{vap}, °C), optimal atomization temperatures (T_{at}, °C) and characteristic masses (m_o) obtained for arsenic species with the most efficient combination of chemical modifier and atomizer

Arsenic species	L-Cysteine (g l^{-1})	'End-capped' tube T_{vap}/T_{at} (m_o, pg)		Ir–Zr pre-treated platform in an 'end-capped' tube T_{vap}/T_{at} (m_o, pg)		
		5 μg Pd + 100 μg ascorbic acid	5 μg Pd + 100 μg citric acid	2.5 μg Pd	2.5 μg Pd + 100 μg citric acid	0.2 μg Ir
As(III)	0.005	1400/2300 (18)	1200/2200 (18)	1300/2200 (19)	1400/2300 (17)	1400/2300 (17)
	0.01	1300/2300 (22)	1200/2200 (21)	1300/2200 (20)	1200/2300 (20)	1400/2300 (18)
As(V)	0.005	1400/2300 (18)	1200/2200 (18)	1300/2200 (18)	1400/2300 (17)	1400/2300 (17)
	0.01	1300/2300 (20)	1200/2200 (20)	1300/2200 (20)	1200/2300 (19)	1400/2300 (18)
MMA	0.005	1400/2300 (18)	1200/2200 (18)	1300/2200 (19)	1400/2300 (17)	1400/2300 (17)
	0.01	1200/2300 (22)	1200/2200 (21)	1300/2200 (22)	1200/2300 (20)	1400/2300 (18)
DMA	0.005	1400/2300 (18)	1200/2200 (18)	1300/2200 (19)	1400/2300 (17)	1400/2300 (17)
	0.01	1300/2300 (22)	1200/2200 (21)	1200/2200 (22)	1200/2300 (20)	1400/2300 (18)

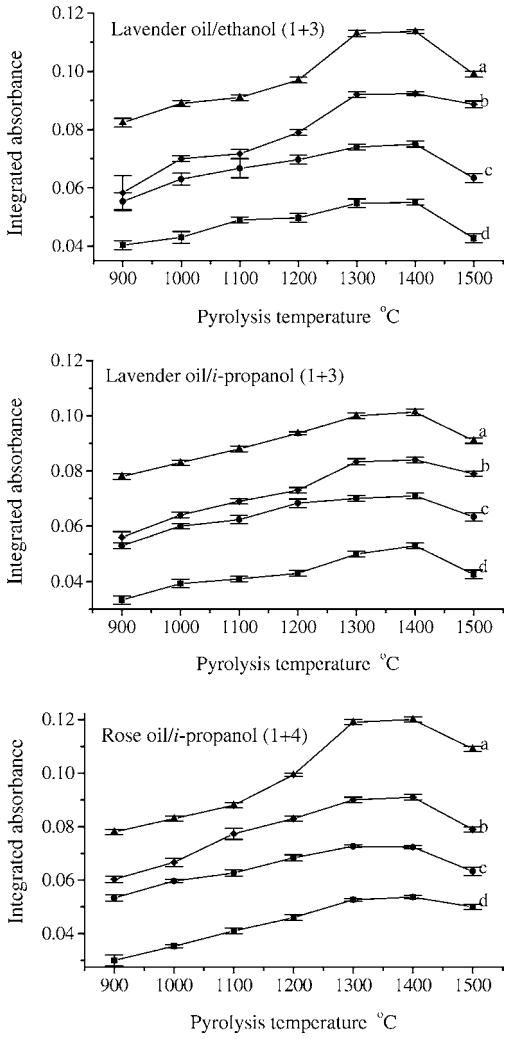

Fig. 1. Pyrolysis curves for DMA in lavender oil diluted in ethanol or *i*-propanol and in rose oil diluted in *i*-propanol with different modifiers: (a) 2.5 μg Pd with 100 μg citric acid on Ir–Zr treated platform; (b) 2.5 μg Pd on Ir–Zr treated platform; (c) 0.2 μg Ir on Ir–Zr treated platform and (d) 5 μg Pd with 100 μg ascorbic acid in an 'end-capped' tube.

The most effective modifier combination is Pd with citric acid. Thermal stabilization up to 1300 °C was achieved for all arsenic species in the presence of lavender or rose oil at relatively low modifier levels (5 μg Pd with 100 μg citric acid) which permits: (i) maximal removal of matrix components and (ii) low temperature atomization of arsenic, better shapes of absorbance–time peaks and lower background absorption. The attempt to increase the amount of Pd did not bring substantial improvement: up to 10 μg Pd plus 100 μg citric acid allows loss-free ashing at 1400 °C but then higher atomization temperature should be used and after all the profile and peak area are impaired. It could be concluded that for these matrices excessive modifier amounts lead to overstabilization of the analyte and of matrix components, resulting in sensitivity reduction and shorted lifetimes of graphite tubes.

Parameters, which should be also carefully optimized when organic diluents are employed are the injection temperature and ramp and hold times for drying and ashing steps. Experiments performed have shown that using a mild 'hot injection' mode at temperature of 30 °C and a two-stage drying at 80 °C for 20 + 10 s and 130 °C for 10 + 10 s ensured smooth drying, better precision and less spreading of sample on platform. Faster heating rates applied during the drying step result in sample boiling, splashing and precision impairment.

A preference to a single-step ashing of essential oils is given, and ramp/hold times of 20 + 30 s were finally adopted (Table 1). Longer hold times do not bring improvement in matrix removal, neither does an intermittent 'cool-down step' before atomization.

3.3. Calibration studies

Matrix effect of multiplicative character have been quantitatively represented as a ratio of the sensitivities (slopes) of standard addition graphs for diluted lavender or rose oil and solvent-matched standard calibration graphs for each one of arsenic species at different ETAAS conditions: in the presence and absence of 0.05 g l^{-1} L-cysteine, Pd with citric acid as modifier and Ir–Zr treated platform as atomizer. Each graph was plotted with three points and each point with three replicates. Different lavender and rose oil dilution factors in ethanol and *i*-propanol or only *i*-propanol were examined in order to elaborate the most suitable calibration procedure. Results are summarized in Table 3. Ethanol is the most suitable solvent for lavender oil analysis. Higher ratios, i.e. lower matrix interferences with almost identical values for different arsenic species were obtained in the presence of 0.05 g l^{-1} L-cysteine for both matrices. Sample dilutions 1 + 3 for lavender oil and 1 + 4 for rose oil allowed calibration with aqueous As(III) or As(V) standards diluted in respective organic solvent, ethanol or *i*-propanol (for lavender and rose oil, respectively). Lower dilution factors call for standard addition calibration. Spike recoveries of different As species range within 95–98%.

3.4. Essential oil digestion

The low temperature oxygen plasma ashing was tested in this study as an effective method for complete dry ashing of essential oil matrix, without significant analyte losses. The radio frequency power and oxygen flow rates were optimized with oil sample mass of 0.3 g. Complete oil ashing was achieved in 1 h and recoveries obtained for all four arsenic species in spiked lavender and rose oil samples varied between 97–99%.

Pressurized wet digestion was performed in small quartz vials inserted in PTFE autoclaves for microwave digestion using HNO_3 or mixture of HNO_3 and H_2O_2. The optimal mass of oil sample is 0.2 g, with 2 ml of HNO_3 and 1 ml of 30% H_2O_2. The absence of hydrogen peroxide entails in-

Table 3
The ratios of the slopes (b) of calibration curves (mean ± S.D.; n = 3)

Oil sample and dilution factor	Arsenic species	b_1/b_0	b_2/b_0
Lavender oil (1:2 with ethanol)	As(III)	0.85 ± 0.03	0.85 ± 0.04
	As(V)	0.85 ± 0.03	0.84 ± 0.04
	MMA	0.84 ± 0.03	0.80 ± 0.04
	DMA	0.84 ± 0.03	0.80 ± 0.05
Lavender oil (1:2 with *i*-propanol)	As(III)	0.81 ± 0.04	0.80 ± 0.05
	As(V)	0.80 ± 0.05	0.76 ± 0.05
	MMA	0.80 ± 0.04	0.75 ± 0.05
	DMA	0.80 ± 0.05	0.78 ± 0.05
Lavender oil (1:3 with ethanol)	As(III)	0.99 ± 0.02	0.99 ± 0.03
	As(V)	0.99 ± 0.02	0.97 ± 0.04
	MMA	0.98 ± 0.02	0.96 ± 0.03
	DMA	0.98 ± 0.02	0.95 ± 0.03
Lavender oil (1:3 with *i*-propanol)	As(III)	0.95 ± 0.03	0.94 ± 0.04
	As(V)	0.94 ± 0.04	0.94 ± 0.04
	MMA	0.95 ± 0.03	0.90 ± 0.04
	DMA	0.94 ± 0.03	0.90 ± 0.04
Rose oil (1:3 with *i*-propanol)	As(III)	0.85 ± 0.04	0.85 ± 0.05
	As(V)	0.86 ± 0.04	0.81 ± 0.05
	MMA	0.85 ± 0.04	0.80 ± 0.05
	DMA	0.85 ± 0.04	0.79 ± 0.05
Rose oil (1:4 with *i*-propanol)	As(III)	0.96 ± 0.02	0.95 ± 0.03
	As(V)	0.96 ± 0.02	0.94 ± 0.04
	MMA	0.95 ± 0.03	0.90 ± 0.04
	DMA	0.95 ± 0.03	0.90 ± 0.04

b_0: The slope of solvent-matched calibration graph (standard solutions in ethanol or *i*-propanol, as appropriate for particular type of oil); b_1: the slope of matrix-matched and solvent-matched calibration graph in the presence of 0.05 g l^{-1} L-cysteine and b_2: the slope of matrix-matched and solvent-matched calibration graph in the absence of L-cysteine.

complete digestion because of carbonization. It is realized that bomb decompositions are prone to incomplete digestion of the organic matter and of certain persistent organoarsenicals [27,28], nevertheless this clean, loss-free decomposition has been applied for elimination of bulk organic matrix and comparison purposes.

3.5. Figures of merit

The limits of detection and quantification for As determination in lavender and rose oil were calculated from 10 replicate measurements of the blank sample on the basis of 3σ- and 10 σ-criterion, respectively. They are listed in Table 4, together with the respective relative standard deviations at As levels in the range 2–10 ng g^{-1}. Comparative results from parallel analysis of two lavender and one rose oil samples are shown in the same table. There is a good agreement between results based on different sample treatment approaches.

4. Conclusions

The ETAAS determination of arsenic in essential oils can be carried out by direct injection of samples diluted in ethanol (lavender oil) or *i*-propanol (rose oil) in the presence of L-cysteine as isoformer, Pd with citric acid as modifier and 'end-capped' graphite tube with permanently Zr–Ir treated platform as atomizer. Calibration by means of aqueous standard solutions of As(III) diluted in ethanol or *i*-propanol could be used for 1 + 3 diluted lavender oil or 1 + 4 diluted rose oil samples, respectively. Lower dilution factors call for standard addition calibration. Direct ETAAS procedure is fast, sensitive and accurate for implementation in the routine control of

Table 4
Figures of merit

Parameter	Direct ETAAS of diluted samples		ETAAS of dry ashed (LTA) samples		ETAAS of wet digested samples	
	Lavender oil	Rose oil	Lavender oil	Rose oil	Lavender oil	Rose oil
Limit of detection (ng g^{-1})	4.4	4.7	2.5	2.7	7.0	7.1
R.S.D. (%)	8–15	9–17	8–12	10–12	15–19	15–20
Arsenic content (ng g^{-1}; mean ± S.D.; n = 3)	Oil A < 4.4; oil B 5.9 ± 0.3	Oil C 5.1 ± 0.3	Oil A < 2.5; oil B 5.7 ± 0.2	Oil C 4.9 ± 0.2	Oil A < 7; oil B < 7	Oil C < 7

essential oils. Procedure involving low temperature oxygen plasma ashing provides better limits of detection and better precision.

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