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Analytical Methods

# Rapid screening of water soluble arsenic species in edible oils using dispersive liquid–liquid microextraction

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ABSTRACT

A methodology for the non-chromatographic screening of the main arsenic species present in edible oils is discussed. Reverse dispersive liquid–liquid microextraction was used to extract water soluble arsenic compounds (inorganic arsenic, methylarsonate, dimethylarsinate and arsenobetaine) from the edible oils into a slightly acidic aqueous medium. The total arsenic content was measured in the extracts by electrothermal atomic absorption spectrometry using palladium as the chemical modifier. By repeating the measurement using cerium instead of palladium, the sum of inorganic arsenic and methylarsonate was obtained. The detection limit was 0.03 ng As per gram of oil. Data for the total and water-soluble arsenic levels of 29 samples of different origin are presented. Inorganic arsenic was not found in any of the samples marketed as edible oils.



## 1. Introduction

The need to know the exact nature and behaviour of the different arsenic compounds present in the environment and in foods does not need to be emphasised (Cornelis, Caruso, Crews, & Heumann, 2005). However, this is not an easy task since the element is ubiquitous, its chemistry complex (giving arise to a large number of compounds, especially in foods), and it is often found in low concentrations that hinder interpretation of any analytical data obtained (Francesconi & Kuehnelt, 2002; Rumpler et al., 2008). When dealing with foods, measurement of the total arsenic content is necessary but not necessarily sufficient, for risk assessment since the toxicity of the different species varies widely. The usual way of measuring the total content of this element in foods involves mineralisation of the sample before using a sensitive analytical technique such as hydride generation atomic absorption spectrometry (HG-AAS), atomic fluorescence spectrometry (HG-AFS) or inductively coupled plasma mass spectrometry (ICP-MS) (Chen, Lee, Cheng, & Chou, 2001; Delgado-Andrade, Navarro, López, & López, 2003; Kohlmeyer, Jakubik, Kuballa, & Jantzen, 2005). However, even these sensitive analytical techniques are not sufficiently sensitive for some purposes since the dissolution stage involves dilution. Alternative choices to total dissolution include the use of emulsions or direct introduction into the electrothermal atomizer of an atomic absorption spectrometer (ETAAS), although sensitivity still remains a drawback (Chen, Cheng, & Chou, 2003; Karadjova & Venelinov, 2002).

The difficulties involved in measuring low levels of arsenic are further increased if speciation is to be carried out since the total amount is distributed across a wide variety of arsenic compounds. This means that, in practice, ICP-MS is required, usually in conjunction with a chromatographic technique (Chu & Jiang, 2011; Schmeisser, Goessler, Kienzl, & Francesconi, 2005). The analytical superiority in terms of sensitivity of ICP-MS over other analytical methods is unquestionable, but it is expensive both as regards acquisition and maintenance.

Edible oils obtained from fish are recommended as nutritional supplements because some components have benefits in human health, although they represent a possible source of arsenic intake since the element accumulates in the marine environment (Francesconi, 2010). There are abundant studies reporting levels of arsenic in these food/supplements, due to the complex chemistry involved (Devallay & Feldmann, 2003; Rumpler et al., 2008; Taleshi et al., 2008, 2010). The relevance of the subject, therefore, is beyond doubt and the approach here presented tackles it from a particular point of view.

This contribution describes our studies using dispersive liquid–liquid microextraction (DLLME) for the isolation of water-soluble arsenic species present in edible oils of animal or plant origin. DLLME, which was introduced several years ago (Rezaee et al.,

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2006), represents an environmentally friendly methodology since it uses minimal amounts of organic reagents. Usually DLLME involves the extraction of analytes from an aqueous phase (the sample) into a small volume of organic phase in the presence of a third solvent that aids rapid and efficient dispersion (Escudero, Martinis, Olsina, & Wuilloud, 2013; Pena-Pereira, Lavilla, & Bendicho 2010; Rivas, López-García, & Hernández-Córdoba, 2009). In this work the technique was used in the opposite way; analytes were extracted from an organic phase (oil samples) into the aqueous phase. In this way, pre-concentration was achieved and the reliability of the analytical data improved. In addition ETA-AS, an analytical technique that is available worldwide, was used for the final analysis. The pre-concentration effect inherent in DLLME increased the sensitivity of the final measurement. Appropriate selection of the experimental conditions allows discrimination between the most toxic inorganic arsenic species and the less toxic compounds (mainly, but not exclusively, arsenobetaine) without the need for a chromatographic stage (López-García, Briceño, & Hernández-Córdoba, 2011). Complete speciation was not possible but a reliable and relatively easy-to-perform assessment of the toxicity of the water-soluble arsenic compounds present in edible oils was achieved.

## 2. Materials and methods

### 2.1. Instrumentation

All the atomic absorption measurements were carried out with a model 800 spectrometer (PerkinElmer, Waltham, MA) equipped with a transversely heated graphite atomizer, Zeeman-effect background correction device and autosampler (model AS-800). Pyrolytic graphite platforms inserted into pyrolytically coated tubes were obtained from the same manufacturer. Argon flowing at 250 mL/min was the inert gas. An electrodeless discharge lamp (PerkinElmer) operated at 300 mA was used as the radiation source. The instrumental parameters are summarised in Table 1.

**Table 1**
Instrumental parameters and experimental conditions for As determination in the DLLME extracts.

| Parameter | Value |
|---|---|
| EDL lamp current (mA) | 300 |
| Wavelength (nm) | 193.7 |
| Spectral band width (nm) | 0.7 |
| Atomizer type | Platform |
| Injected sample volume (μL) | 30 |
| Chemical modifier[a] | 0.3 μg Ce(IV); 20 μg Pd |
| Calibration graph (μg $L^{-1}$) | 2–100 |
| Acceptor phase (μL) | 300 (76% isopropyl alcohol + 0.7% $HNO_3$) |
| Donor phase (g) | 10 |
| Limit of detection in oil (ng $g^{-1}$) | 0.03 ng $g^{-1}$ |
| RSD (%) | <4.6 |

| Step | Temperature (°C) | Ramp (°C/s) | Hold (s) |
|---|---|---|---|
| *Furnace heating program* | | | |
| 1: Dry | 90 | 1 | 20 |
| 2: Dry | 130 | 1 | 30 |
| 3: Ash | 400 | 10 | 30 |
| 4: Ash | 800 | 5 | 30 |
| 4: Atomization[b,c] | 2300 | 0 | 4 |
| 5: Clean | 2600 | 0 | 3 |
| *Sequence for arsenic determination* | | | |
| A | Pipette 20 μL of the modifier and run step 1 and 2 | | |
| B | Inject the sample and run the entire program | | |

[a] See the text for details.
[b] Flow of argon stopped.
[c] Reading step.

The hydride generation atomic fluorescence spectrometric (HG-AFS) measurements were carried out with a Millennium Excalibur spectrometer (PS Analytical, Orpington, UK) operating in continuous flow mode, and the analytical signal obtained at 197.3 nm. For HG-AFS, a solution containing 3.5 mol/L hydrochloric acid, 1% (m/v) potassium iodide and 0.2% (m/v) ascorbic acid was pumped at 9.0 mL/min and a reducing solution containing 0.6% (m/v) sodium tetrahydroborate stabilized with sodium hydroxide (0.075 mol/L) was run at 4.5 mL/min. Argon was used as the carrier.

For comparison purposes, complete digestion of the samples was carried out with a Multiwave 3000 microwave digestion system (Anton Paar, Austria). A 50 W ultrasound bath (ATU, Valencia, Spain) was used for the ultrasonic treatment.

### 2.2. Reagents and samples

Pure water (18 MΩ cm resistivity) obtained with a Millipore system (Millipore, Bedford, MA) was used exclusively. To prevent contamination, all glassware was washed with 10% (v/v) nitric acid and then rinsed with water before use. The inorganic arsenic standard solutions (1000 μg/mL) were prepared from $NaAsO_2$ and $Na_2HAsO_4$ (Fluka, Buchs, Switzerland) and stored in PTFE bottles at 4 °C. The dimethylarsinic acid ($(CH_3)_2As(O)OH$, DMA, Sigma, St. Louis, MO, USA) and sodium methylarsonate ($CH_3AsO(ONa)_2{\cdot}6H_2O$, MA, Carlo Erba, Milan, Italy) solutions, containing 1000 μg/mL arsenic, were prepared in water and stored in the same way. Diluted solutions were prepared daily. The arsenobetaine (AB) standard solution was obtained from the Institute for Reference Materials and Measurements (IRMM). This reference material (BCR CRM 626) had a certified AB content of 1031 ± 6 μg/g corresponding to 433 ± 3 μg/g arsenic. HLB solid-phase cartridges (6 mL, 200 mg) were obtained from Supelco (Bellefonte, PA, USA). The rest of the chemicals used were obtained from Fluka or Sigma.

Commercial edible oils, labelled as olive, extra virgin olive, olive pomace, sunflower, maize, soy, seed, avocado, walnut and macadamia, were acquired in local supermarkets. In the case of canned fish (sardine, tuna, mackerel and anchovy) prepared in olive or sunflower oil, only the oil was used for analysis. Other oils were obtained in specialised markets or parapharmacies where they are marketed as nutritional supplements (primrose, wheat germ, salmon, cod liver and fish oils). In addition, five samples marketed by Sigma, namely F8020 (fish oil from menhaden), 74380 (fish liver oil from *Gadus Morhua*), 85067 (sesame oil from *Sesamum indicum*), P1244 (peanut oil) and C8267 (corn oil) were used.

To check the reliability of both the standard solutions used for calibration and the results obtained, several standard reference materials were also analysed. DORM-2 (dogfish muscle) and DORM-4 (fish protein) were obtained from the National Research Council of Canada (NRC-CNRC, Ottawa, Ontario, Canada), while SRM 1568a (rice flour) and 1566a (oyster tissue) were provided by the National Institute of Standards and Technology (NIST, Gaithersburg, MD). Although the certificates of these samples refer only to the total arsenic content, values for the different arsenic species they contain were found in the literature.

### 2.3. Analytical procedures

For the HG-AFS determination of total arsenic content, the oil samples were first mineralised. To this effect, 0.25 g sample were digested in a microwave oven with a solution consisting of hydrogen peroxide, and nitric and hydrochloric acids; the resulting solution was made up to 25 mL with 3.5 mol/L hydrochloric acid. Samples were subjected to analysis using solutions containing arsenic (0.1–2 μg/L) for calibration. The detection limit (LOD, three