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Short communication

Simultaneous extraction and derivatization of 2-chlorovinylarsonous acid from soils using supercritical and pressurized fluids

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Abstract

Supercritical carbon dioxide and pressurized fluids are compared for the extraction with in situ derivatization of 2-chlorovinylarsonous acid (CVAA) from a series of seven spiked soils. Samples are allowed to age (up to 42 days) and periodically extracted. Sample ageing leads to a recovery decrease due to the development of strong interactions between CVAA and matrix active sites, as time elapses. A similar behavior is observed when usual ultrasonic extraction is performed. Supercritical fluid extraction (SFE) with in situ derivatization leads to the highest recovery. Moreover, SFE allows a solvent consumption reduction. A limit of detection of 0.2 μg/g is reached with the SFE method.

Keywords: Derivatization, SFE; Supercritical fluid extraction; 2-Chlorovinylarsonous acid

1. Introduction

Lewisite L I (2-chlorovinyldichloroarsine) is a highly toxic arsenical compound of historical military interest [1,2]. On contact with moisture, Lewisite L I leads to 2-chlorovinylarsonous acid (CVAA) [3,4]. Consequently, for mapping out possible contaminated areas (former manufacturing, storage areas, etc.), a CVAA-dedicated method is required.

In previous work, CVAA has been determined as 2-(2-chlorovinyl)-1,3,2-dithiarsenoline (CDA) by gas chromatography following derivatization with 1,2-ethanedithiol. Initially, solvent extraction was used [3] but more recently solid-phase microextraction (SPME) has enabled the detection limit to be lowered to 2 μg/l [5].

However, CVAA determination in solid matrices requires one additional extraction step which up to now, has been performed by ultrasonic extraction (USE). We report here the possibility to replace this tedious and time-consuming method by supercritical fluid extraction (SFE) or accelerated solvent extraction (ASE) with in situ derivatization.

In the first case (SFE), 1,2-ethanedithiol is added to the matrix before performing extraction and the derivatization reaction occurs in supercritical fluid medium during a static step [6,7]. In the second case (ASE), reagent is added directly into the extraction solvent. According to our knowledge, it is the first

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time that ASE with in situ derivatization is implemented.

First, SFE and ASE with in situ derivatization are applied to freshly spiked soil in order to optimize extraction parameters. After that, an ageing study was performed on a series of seven spiked soils.

2. Experimental

2.1. Chemicals

Lewisite L I (2-chlorovinyldichloroarsine) and 2-(2-chlorovinyl)-1,3,2-dithiarsenoline (CDA) were synthesized at the Centre d'Etudes du Bouchet (French defense research establishment). CDA was obtained from Lewisite by reaction with 1,2-ethanedithiol [8]. 2-Chloroethylphenyl sulfide (purity: 99.4% after distillation of the commercial product) and 1,2-ethanedithiol (purity higher than 98.0%) were purchased from Fluka (Saint Quentin Fallavier, France).

2.2. Solvents and gas

Dichloromethane (Pestinorm grade), ethyl acetate (Pestinorm grade), toluene (Pestinorm grade) and isopropanol (Pestinorm grade) were purchased from Prolabo (Nogent sur Marne, France). Deionized water was freshly prepared by the Alpha-Q water purification system (Millipore, Bedford, MA, USA). Carbon dioxide (purity N48) and nitrogen (purity N60) were provided by Alphagaz (Saint Quentin en Yvelines, France).

2.3. Soil preparation and spiking

Six types of soil were allowed to dry at 40°C for a week and sieved at 2 mm before being spiked. The local soil was collected close to our laboratory. Podzol, rendzine, sedimentary clay, silt and cultivated soil were received from the French National Institute of Agronomic Research (INRA, Olivet, France).

The spiking solution was prepared by mixing 10 ml of deionized water with 10 ml of a 8 μl/ml Lewisite L I solution in isopropanol (formation of CVAA by hydrolysis of Lewisite L I). Soil spiking was performed as follow. A 150-g amount of soil was placed in a 250-ml Erlenmeyer flask. Then, 360 μl of spiking solution was added and the resulting mixture was agitated during 2 min with a vortex mixer. After a 30-min waiting period, the soil was again agitated during 2 min. Then, the screw-capped vessel was closed and the soil was stored at room temperature until the extraction procedure.

2.4. Supercritical fluid extraction

Chemical derivatization–SFE was performed in a two-step manner. First, CVAA derivatization occurs during a 10-min static period. After that, CDA (product of the derivatization reaction) is extracted under dynamic conditions (CO_2 flow-rate: 1 ml/min, duration: 20 min). All the SFE experiments were carried out in triplicate using a HP 7680A supercritical fluid extractor (Hewlett-Packard, Les Ulis, France). The sample was accurately weighed (between 10 and 11 g per cell) into the 7-ml extractor thimble and 1,2-ethanedithiol added to the top of the cell just before starting the extraction.

Before performing extraction, 700 μl of modifier (methanol, toluene or diethylamine) may also be added to the top of the cell.

After each extraction, 30 μl of a 5.0 mg/ml 2-chloroethylphenyl sulfide solution in ethyl acetate (internal standard) was added to the extract.

The extractor trapping system was modified as previously described [9] in order to check the trap efficiency. During the extraction of a CVAA freshly spiked sand (80°C, CO_2 density: 0.60 g/ml, addition of 50 μl of 1,2-ethanedithiol and 700 μl of methanol in the cell just before the extraction), it was shown that all extracted compounds are collected in the trap (trapping material: Isolut ENV+). The same result was reached when toluene or diethylamine were used instead of methanol. Indeed, as previously described, the solid trapping remains efficient when modifier is added to supercritical CO_2 provided that a high specific area polymeric phase is used instead of a classical octadecyl silica [10].

Moreover it was also shown that 1.5 ml is the lowest volume of ethyl acetate which allows a total elution of solutes from the trap.

2.5. Accelerated solvent extraction

Extractions were performed with a Dionex ASE 200 system (Dionex, Jouy en Josas, France). Samples were accurately weighed (between 14 and 15 g) into the 11-ml cell. A cellulose filter (diameter: 19.1 mm, type D28) supplied by Dionex was routinely disposed at the exit of the cell to prevent clogging of the metal frit. Extraction starts with a filling step: the extracting mixture (AcOEt+1,2-ethanedithiol at a concentration of 0.02, 0.04 or 0.09 μl/ml) is pumped through the cell. When the cell is full and the collection vial contains about 1 ml of extracting mixture, the static valve is closed and the pump is automatically stopped. Then a static extraction step occurs (100 bar). Thereafter, the static valve is opened and the cell is percolated with fresh extracting mixture (from 1 to 20 ml). The two former steps (static extraction and flushing) are repeated up to three times. Finally, the extraction cell is purged with nitrogen (180 p.s.i.) during 1.5 min to assure a complete solvent transfer to collection vial (1 p.s.i.= 6894.76 Pa). After each extraction, 42 μl of a 5.0 mg/ml (2-chloroethyl)phenyl sulfide solution in ethyl acetate (internal standard) was added to the extract.

2.6. USE–derivatization–liquid–liquid extraction

The usual technique for extracting CVAA from soil is shown in Fig. 1.

2.7. Gas chromatography

The extracts were quantitatively analyzed in triplicate on a Varian 3400 gas chromatograph (Varian, Les Ulis, France) equipped with a flame ionization detection (FID) system, a split/splitless injector (Varian 1077) and an autosampler (Varian 8200). A RESTEK Rtx-5MS (5% biphenyl, 95% methylpolysiloxane) with an integrated guard column was used (30 m×0.32 mm I.D., film thickness of 0.25 μm). The autosampler injections (1 μl) were performed in the splitless mode for 0.75 min. The oven temperature was held at 50°C for 1 min then ramped to 260°C at 10°C/min. The injector and detector temperatures were set at 250°C and 260°C, respectively. Linear correlation coefficients (r^2) for all calibration curves were always greater than 0.995.

3. Results and discussion

3.1. Supercritical fluid extraction and derivatization of CVAA from freshly spiked soil

3.1.1. Temperature

CVAA extraction efficiency from freshly spiked soil is represented in Table 1.

When pure carbon dioxide extraction is conducted on local soil at 40°C, CVAA recovery is 58.2% (introduction of 10 equiv. of 1,2-ethanedithiol). This poor recovery is due to analyte–matrix interactions which inhibit the extraction process (with the same experimental conditions, extraction of CVAA from calcined sea sand – a inert matrix – is quantitative). Since increasing temperature has been found to be a very effective strategy for increasing extraction efficiencies of analytes tightly bound to the sample matrix [11,12], temperatures up to 120°C (maximum value of the instrument) were implemented. Unfortunately, such a temperature increase was not sufficient to remove target compound from matrix binding sites (Table 1) and leads even to a recovery decrease probably due to 1,2-ethanedithiol self condensation [resultant compounds were evidenced by gas chromatography–mass spectrometry (GC–MS)].

3.1.2. Modifier addition

In order to increase extraction recovery, addition of modifier to supercritical carbon dioxide was considered. Since extraction is primarily limited by analyte–matrix interactions, the major goal of the modifier is to interact with matrix active sites (enhancement of analyte removal from binding sites) rather than to increase analyte solubility (extractions on sea sand have shown that CDA solubility in supercritical CO_2 is high enough to lead to its total solubilization). Since the nature of interactions between the target compounds and the matrix is not known, the best approach is to determine the relative performance of modifiers with different polarity characteristics, i.e., testing methanol, diethylamine and toluene [13,14]. Diethylamine and toluene addition does not give an increasing recovery. Methanol

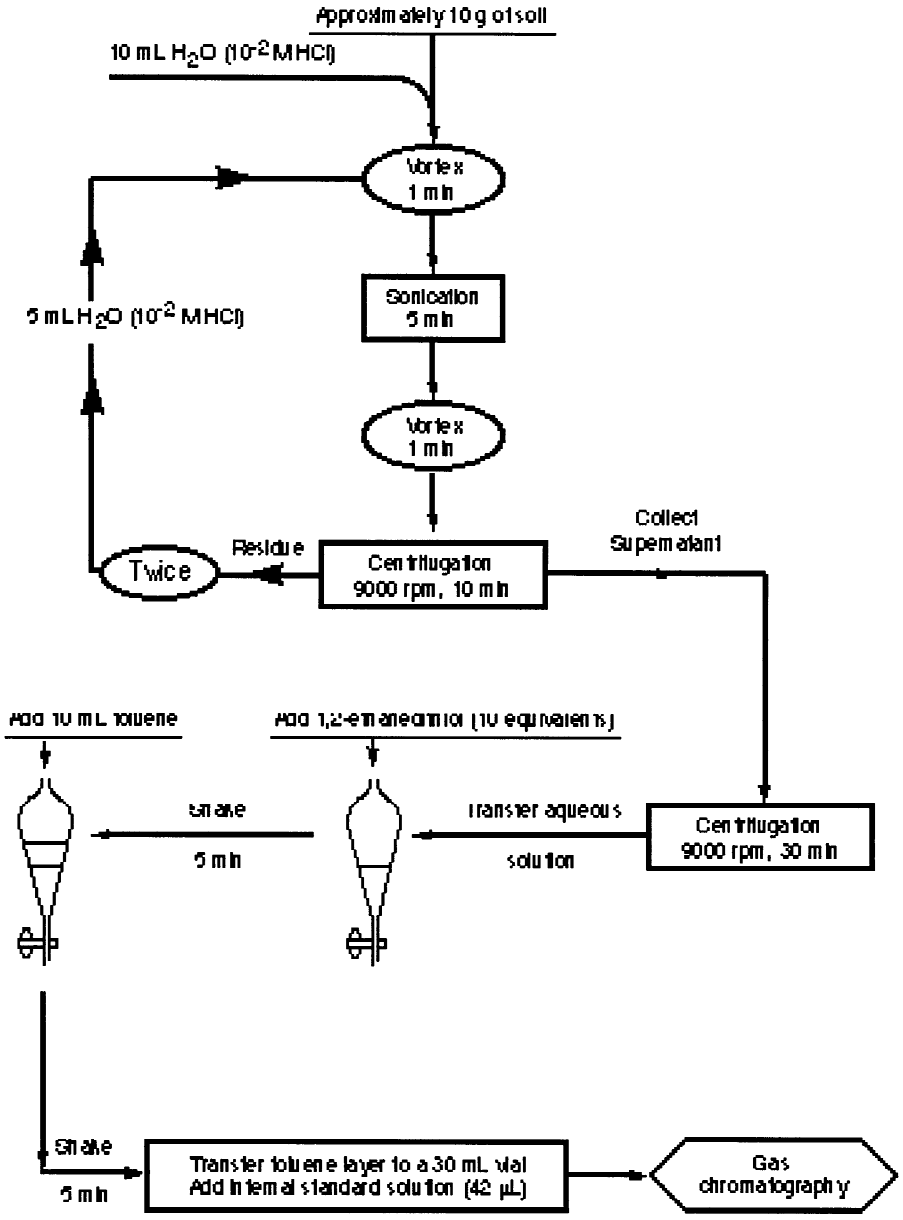

Fig. 1. Ultrasonic extraction–derivatization–liquid–liquid extraction methodology.

addition is much more efficient: extraction recovery increases from 55.6% to 71.1% at 80°C (Table 1). Therefore, further supercritical fluid extractions will be performed at 80°C in the presence of methanol (700 µl, i.e., 10% of the extraction cell volume).

3.1.3. Stoichiometry

In order to increase extraction efficiency, a larger amount of 1,2-ethanedithiol was added to the sample (600 equiv., i.e., 50 µl of pure 1,2-ethanedithiol).

The large excess of 1,2-ethanedithiol was consid-

Table 1
Modifiers, 1,2-ethanedithiol stoichiometry and temperature influence on CVAA extraction efficiency from local soil (extraction conditions: CO_2 density: 0.60 g/ml)[a]

Temperature (°C)	Pure CO_2, 10 equiv. 1,2-ethanedithiol	CO_2+700 μl MeOH	
		10 equiv. 1,2-ethanedithiol	600 equiv. 1,2-ethanedithiol
40	58.2 (2.0)	70.1 (1.8)	–
80	55.6 (2.0)	71.1 (3.8)	83.5 (3.2)
120	42.1 (2.2)	64.2 (0.7)	–

[a] Values in parentheses are relative standard deviations (n=3).

ered to act by displacement of CVAA molecules from polar active sites of the matrix. In this way, CVAA recovery increases up to 83.5% (Table 1).

Therefore, 50 μl of 1,2-ethanedithiol will be added to the sample and a static step of 10 min will be implemented (it was shown that an increase of static step from 10 to 30 min does not lead to an increase of CVAA extraction efficiency).

3.2. Accelerated solvent extraction and derivatization of CVAA from freshly spiked soil

3.2.1. Temperature

Extraction efficiency of CVAA from spiked local soil is not quantitative (64%). Indeed, matrix active sites can develop interactions with target compound, leading to a difficult extraction step (under the same conditions, extraction of CVAA from calcined sea sand – a inert matrix – is quantitative).

Unfortunately, increasing temperature (up to 200°C) does not lead to a better extraction efficiency despite an increase of thermal energy versus matrix–target compound interactions. Therefore, further accelerated solvent extractions with in situ derivatization will be implemented at 80°C (a temperature decrease entails a decreasing recovery). It was checked that the nitrogen purge (1.5 min–180 p.s.i.) was sufficient to assure a complete solvent transfer to the collection vial. Moreover, it was also checked that, as it was already described elsewhere [15,16], pressure has no influence on the extraction efficiency.

3.2.2. Number of cycles – flush volume

Up to now, all accelerated solvent extractions were performed in one cycle (one static period). A three-cycle extraction (three static periods of 10 min with introduction of fresh extracting mixture – 33% of the total cell volume – at the beginning of each static period) leads to a more efficient extraction: recovery increases up to 85.6%.

Therefore, further extractions will be implemented in three cycles of 10 min.

3.3. Comparison of SFE, ASE and USE

3.3.1. SFE

It is well known [17] that sample ageing can greatly reduce extraction recovery (development of interactions between target compounds and matrix active sites). So, seven CVAA spiked soils were allowed to age and periodically extracted. Results are represented in Fig. 2. First, it appears that SFE with in situ derivatization efficiency depends of the soil type. In addition, sample ageing leads to a sizable decrease in recovery (excepted for calcined sea sand).

Each 21-day-old sample extracted by supercritical carbon dioxide was re-extracted by nitric acid (5 *M*) for 1 h under reflux (arsenic contained in extracts is analyzed by atomic absorption). This re-extraction allows one to recover missing arsenic corresponding to CVAA unextracted by SFE. SFE with in situ derivatization conditions is therefore not strong enough to remove CVAA from binding sites of the matrix. We must point out that, for a real sample, univocal identification of Lewisite L I pollution cannot be performed by nitric acid extraction (arsenic revealed by this method can be the result of another arsenical compound pollution). The SFE

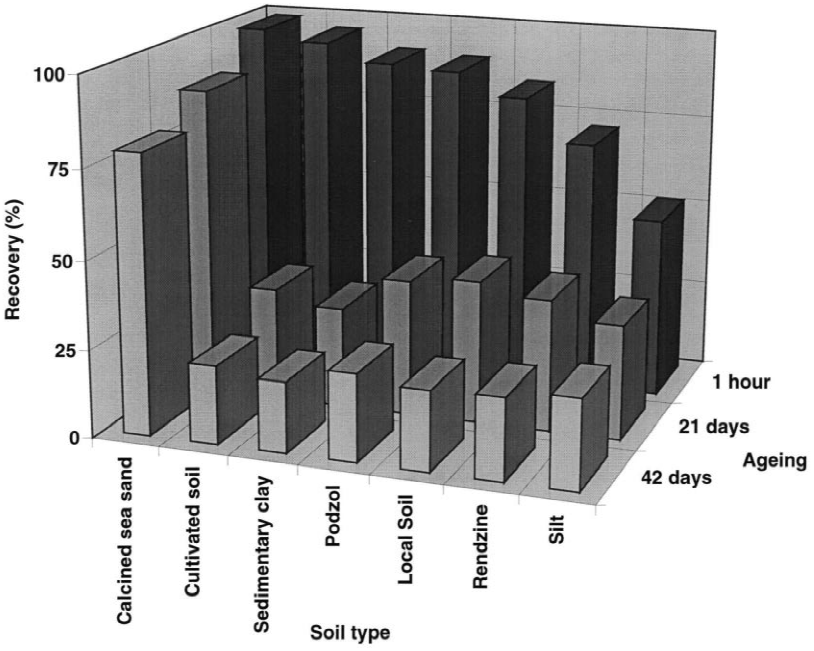

Fig. 2. SFE with in situ derivatization of CVAA spiked onto seven soils as a function of ageing (extraction conditions: 80°C, CO_2 density: 0.60 g/ml, homogeneous addition of 50 μl of 1,2-ethanedithiol, addition of 700 μl of methanol).

method has the advantage of allowing an undoubted identification of Lewisite L I by GC–MS analysis of CDA. After having revealing a Lewisite L I pollution by means of SFE–GC–MS, the maximum pollution level can be estimated by performing a nitric acid extraction under reflux.

3.3.2. ASE

Similarly to SFE, the development of interactions between CVAA and matrix active sites leads to a decrease of ASE recoveries when samples age. However, ASE gives slightly lower recoveries than SFE.

3.3.3. USE

This technique was applied to the seven matrices studied previously. Some samples are very difficult to extract by ultrasonic extraction. For instance, water addition to sedimentary clay leads to the formation of a very viscous mud. This mud sticks to the vial wall during the first centrifugation step. During the addition of the next 5 ml of water (10^{-2} *M* HCl), the mud stays to the vial wall and consequently recovery obtained is low (poor contact between water and clay).

4. Conclusion

From the three methods considered, SFE is the one which leads to the highest recoveries. However, sample ageing entails a tremendously recovery decrease due to the development of strong interactions between target compound and matrix active sites.

SFE is the fastest method (40 min vs. 50 min and 150 min for ASE and USE, respectively) and allows the lowest solvent consumption (1.5 ml of ethyl acetate vs. 18 ml of ethyl acetate and 10 ml of toluene for ASE and USE, respectively).

After an undoubted identification of Lewisite L I pollution by means of GC–MS analysis of CDA contained in SFE extract, a complementary nitric acid extraction (1 h under reflux, 5*M*) can be implemented to estimate the maximum concentration of CVAA in sample (this latter method allows a quantitative extraction of CVAA, but also native arsenic and possible other arsenical compounds).

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