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Identification of degradation products of phenylarsonic acid and *o*-arsanilic acid in contact with suspensions of soils of volcanic origin

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ABSTRACT

A set of organoarsenicals were identified in aqueous phenylarsonic acid (PA) and *o*-arsanilic acid (AA) solutions treated with soil of volcanic origin in batch systems. The transformation products were separated by liquid chromatography (RP-LC) and identified with element selective inductively coupled plasma-mass spectrometry (ICP-MS) as well as molecular selective electrospray ionization-mass spectrometry (ESI-MS) detection after their HPLC separation. The identification of the main degradation products by means of ESI-MS, ESI-MS/MS and ESI-TOF-MS showed the occurrence of nitrophenylarsonic acid and methylphenylarsinic acid in the solutions containing AA and PA in contact with soils, respectively. Using irradiation of PA solution with visible light, new compounds related from PA appeared with increasing irradiation times which were identified as 4-hydroxyphenylarsonic acid, 3-hydroxyphenylarsonic acid and 2-hydroxyphenylarsonic acid. Additionally, a dihydroxyphenylarsonic compound was identified as impurity of PA.

1. Introduction

Phenylarsenicals used as chemical warfare agents [1] and animal medication [2] contribute to the environmental pollution around the world. Several phenylarsenicals have been widely used for coccidiosis prevention and animal growth promotion in the poultry industry [3–5], as chemotherapeuticals and effective growth promoter in the swine industry as well [6,7]. In manure roxarsone (RO) and *p*-arsanilic acid can be found in very low concentration as a result of their bioaccumulation and because they are mainly excreted almost unchanged [5]. Arsenate (As^{V}), arsenite (As^{III}), monomethylarsonic acid, dimethylarsinic acid, 3-amino-4-hydroxyphenylarsonic acid and 4-hydroxyphenylarsonic acid have been detected in low concentrations as metabolites in manures [8].

Phenylarsenicals are introduced into the soil when poultry litter is used as fertilizer on cropland [2,9]. RO has shown to be stable in dried poultry litter, but when litter was in contact with water for certain incubation time; arsenate was the main degradation product [10]. In studies carried out with manure amended soil arsenate was the main metabolite of roxarsone, as well [8].

Soils from volcanic origin are widely distributed. They occur under different environmental conditions and might be relevant for countries having this type of soil for agricultural use. Mineral rich soils derived from volcanic loams and volcanic ashes are particularly good for pasture growth, horticulture and maize. In a previous work, we reported that aqueous solution of phenylarsenicals in contact with volcanic soils, produced arsenate (As^{V}), arsenite (As^{III}) and several organic arsenic compounds after 24 h [11,12]. Phenylarsenicals and its degradation products are highly water-soluble, thus they can contaminate groundwater and can sorbed by plants [13]. After it, the conditions are created so that phenylarsenicals and their transformation products enter the human through the nutritional chain [14–18].

Phenylarsenicals can be also transformed by microorganisms into products of higher toxicity and mobility than the original compounds [19–21]. HPLC and capillary electrophoresis techniques are the most suitable separation techniques for these water-soluble arsenic species found in the environment [22,23]. HPLC-MS is the most popular hyphenated technique used so far for arsenic speciation analysis. For studies of elemental and molecular identification, the combination of inductively coupled plasma (ICP) mass spectrometry and electrospray ionization (ESI) mass spectrometry with HPLC is a powerful tool for the identification of unknown arsenic species [11,12,22].

The aim of this investigation was to identify transformation products of phenylarsenic compounds (especially derived from phenylarsonic acid and *o*-arsanilic acid), in contact with soils derived from volcanic materials and degraded from extensive

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agricultural activities, by suitable combinations of element selective and molecular selective mass spectrometric methods. The experiments were performed under simulated environmental conditions by interactions with soils of volcanic origin agriculturally used, water and light.

2. Experimental

2.1. Chemicals and reagents

Phenylarsonic acid (purity 99%), 4-hydroxyphenylarsonic acid and 2-nitrophenylarsonic acid were purchased from TCI Europe; *o*-arsanilic acid ((2-aminophenyl)arsonic acid, purity 98%) was purchased from Sigma. Deionized water (Milli-Q, resistivity 18.2 MΩ cm) was used in all the experiments. Methanol (LiChrosolv®) was obtained from Merck (Darmstadt, Germany). Formic acid and all the other chemicals were obtained from Sigma-Aldrich and Fluka and were of analytical grade and better.

2.2. Soil samples

The soils used in this investigation were from the type loamy clay soil containing considerable amounts of iron oxide. The Mexican soils were derived from volcanic materials: an Acrisol (AT) from Atécuaro in the state of Michoacán (19°34'60"N, 101°10'60"W), resulting from old volcanic ashes, a (TL) from Tlalpan in the state of Tlaxcala (19°16'60"N 99°10'0"W), corresponding to a volcanic tuff and an Andosol (LO) from La Loma in Amanalco de Becerra, state of México (19°15'N, 100°01'W). The soil organic carbon content of these soils were 1.2, 3.1 and 0.3% for Acrisol, *Tepetate* and Andosol, respectively. More chemical composition and physical properties of these soils are reported in more detail elsewhere [11,12]. The soil samples were stored at room temperature in a desiccator in dark vessels.

2.3. Sorption and irradiation experiments

Non-sterilized soils were used in this study. The soils were dried at 100 °C for 24 h, prior to use and then sieved and homogenized. Each 3 mL of deionized water containing *o*-arsanilic acid (743 mg L^{-1} as As) and phenylarsonic acid (743 mg L^{-1} as As) were added individually to each 100 mg soil (dried at 100 °C, size fraction <0.71 mm) without any pH adjustment. The soil/solution suspensions were shaken manually during 5 min and stored in a water bath at 25 °C for 24 h under batch conditions. Afterwards the samples were filtered (RC membrane, 0.45 μm, Sartorius) and centrifuged for 30 min at 13,000 rpm. The supernatants were collected and stored at 5 °C during 12 h for subsequent analysis.

For the visible light irradiation experiments, a 705 UV-digester (Metrohm, Herisau, Switzerland) equipped with a high pressure mercury lamp HBO 500 was used. The light intensity of this lamp was 2850 cd and the average light density amounts 30,000 cd cm^{-2}. The wavelength range used was between 400 and 620 nm. Aqueous solutions (10 mL) of AA and PA (50 ppm each) were filled separately in glass vials of 15 mL, separately, and irradiated for 6 and 24 h, respectively. Aliquots of 1 mL were taken at different time intervals for the kinetic experiment and analyzed by HPLC-ICP-MS.

2.4. Analytical methods

2.4.1. HPLC-ICP-MS/ESI-MS

For arsenic speciation, the samples were analyzed using an HPLC-ICP-MS/ESI-MS equipment consisting of μ-LC Series 1100 (Degasser, binary pump, thermostated autosampler) coupled with ICP-MS 7500 ce and ESI-qMS 6130 in parallel (all Agilent Technologies, Santa Clara, USA) by splitting the mobile phase 1:1 by a T-piece. The injection volume used was 8 μL.

For the identification of the phenylarsenic compounds the ICP-MS peaks at *m/z* 75 (As) were compared with those peaks obtained by the ESI-MS detector after their separation by means of reversed-phase chromatography (column: Jupiter C18 (5 μm, 4.6 × 250 mm, Phenomenex, Inc.); eluent A: 0.1% HCOOH, 0.1% CH_3OH; eluent B: 0.1% HCOOH, 20% CH_3OH). The following eluent composition (gradient) was used: 0–3 min 100% A; 3–20 min 0% A (linear); 20-30 min 0% A; 30–31 min 100% A; 31–35 min 100% A. The conditions for the detection are listed in Table 1.

2.4.2. HR ESI-TOF-MS

For high-resolution mass spectrometry, a micrOTOF (Bruker Daltonics, Bremen, Germany), equipped with an Agilent CE-ESI-MS sprayer kit (G1607A), was used. A mixture of propan-2-ol and water (50:50 v/v) containing 0.2% formic acid served as sheath liquid and was pumped with a flow rate of 3 μL min^{-1} using a syringe pump model KDS 601553 (KD Scientific, Holliston, MA, USA). Sample introduction was performed applying pressure to the sample vial which was connected with the coaxial sheath-liquid sprayer via a short piece of fused silica capillary (50 μm I.D., 360 μm O.D.). As a result a sample flow through the capillary was generated. The parameters for the operation of the micrOTOF system are also summarized in Table 1.

2.4.3. HPLC-ESI-MS/MS

For HPLC-ESI-MS/MS measurements the following equipment was used:

HPLC: Agilent 1100 with autosampler (Agilent Technologies, Santa Clara, USA); ESI-MSMS: Triple Quadrupole LC/MS/MS Mass

Table 1
Parameters for ICP-MS, ESI-MS, ESI-MS/MS and ESI-TOF-MS.

ICP-MS (Agilent 7500ce)	**Conditions**
RF power	1500 W
Plasma gas flow rate	Ar 15 L min^{-1}
Carrier gas flow	0.5 – 0.7 L min^{-1}
Sample depth	6 – 7 mm
Ion monitored	*m/z* 75 (As^+)
ESI-MS (Agilent MSD 6130)	
Polarity	Negative for AA and PA; positive for PA
Capillary voltage	4000 V
Fragmentor voltage	−200 V for AA; −200 and +70 V for PA
Nebulizer pressure	40 psi
Scan range	100–300 *m/z*
Spray temperature	350 °C
Nitrogen flow	11 L min^{-1}
ESI-MS/MS (API 2000)	
Polarity	Negative for AA and PA; positive for PA
Capillary voltage	5000 V
Ion source	Turbolon spray
Collision energy	15 V
Product ion scans	Molecular ions $[M–H]^-$ and $[M+H]^+$ as precursors
Spray temperature	300 °C
ESI-TOF-MS (micrOTOF)	
Polarity	Negative for AA and PA; positive for PA
Capillary voltage	4000 V
End plate offset	500 V
Capillary exit	150 V
Nebulizer gas	(N_2): 0.4 bar
Drying gas	(N_2): 4.0 L min^{-1}
Drying temperature	200 °C
Skimmer	1: −50 V, 2: −23 V
Hexapole voltage	1: −23 V, RF: 100 V
Transfer time	49 μs
Pre-pulse storage	10 μs

Spectrometer API 2000 (Perkin-Elmer Sciex Instruments, Waltham, Massachusetts, USA). The parameters for detection are presented in Table 1.

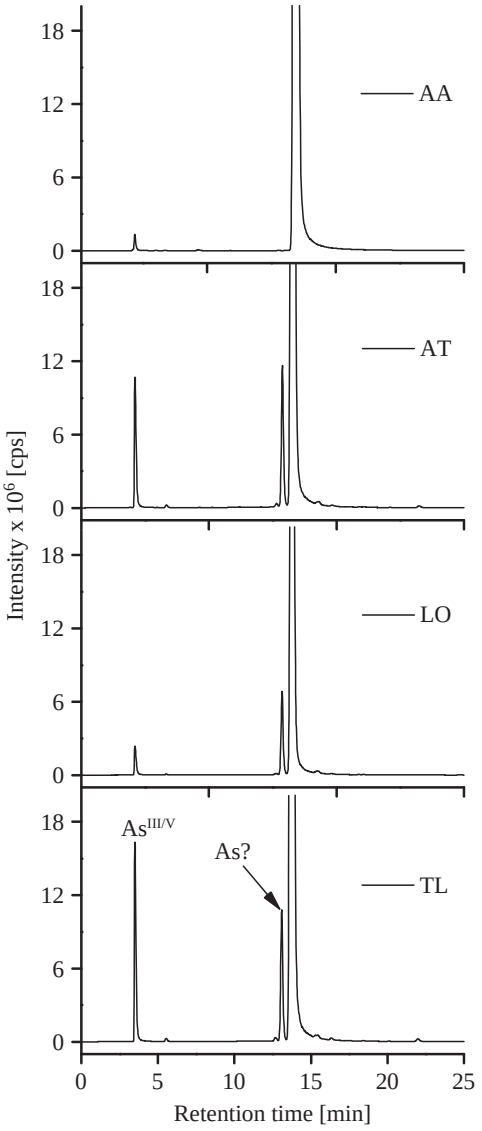

Fig. 1. HPLC-ICP-MS chromatograms of *o*-arsanilic acid (AA) treated with the *Acrisol* (AT), *Andosol* (LO) and *Tepetate* (TL) soils. (iAs) inorganic arsenic and (As?) unknown arsenic species.

2.4.4. Quality control

Blank samples were extracted and analyzed simultaneously with the soil containing samples to determine the potential lability at 25 °C under batch conditions of the phenylarsenicals used in these studies. Beside inorganic arsenic compounds, no organic arsenic compounds were detected in the soils under investigation. All experiments were repeated three times and each sample was also analyzed three times. The total concentrations of arsenic in resulting solutions were determined by ICP-atomic emission spectrometry (CIROS, Spectro, Kleve, Germany).

3. Results and discussion

3.1. Identification of the reaction products of o-arsanilic acid (AA)

Chromatograms (HPLC with ICP-MS detection) of solutions of AA in the initial state and after treatment with an aqueous suspension of the sieved soils AT, LO and TL are shown in Fig. 1. Like in the case of roxarsone [12], additional peaks corresponding probably to transformation products were observed when an aqueous solution of AA was in contact with the soils for a certain time. Besides the formation of inorganic arsenic species ($As^{III/V}$) seen in the peaks within a retention time window of 3 ± 0.5 min smaller peaks are distributed over the whole chromatogram. A particularly intensive peak indicated as appeared in all treated samples shortly before the peak of AA was detected. For this unknown compound with retention time (t_R) 12.73 min an ESI-MS spectrum could be detected simultaneously with a molecular ion mass $[M\text{-}H]^-$ of *m/z* 246 (Fig. 2). This *m/z* value can advert to an oxidation product of AA namely 2-nitrophenylarsonic acid inserted in the MS spectrum of Fig. 2.

In order to support this assumption the accurate molecular mass of the transformation product had to be determined. Therefore, the solution of the AA treated with the soil AT was injected directly (without HPLC separation) in a high resolution ESI-TOF-MS. The ESI-TOF-MS mass spectrum (not shown) in the interval from *m/z* 230 to 300 displayed a signal with a value of *m/z* 245.9386 corresponding well with the result obtained by HPLC-ESI-MS (*m/z* 246) with a mass error of −1.2 ppm calculated to the theoretical molecular mass weight of 2-nitrophenylarsonic acid. HPLC-ESI-MS/MS (Product ion scan) analysis of the selected precursor ion $[M\text{-}H]^- = 246$ indicated the fragment ions with *m/z* 199, 138 and 123 which agreed well with those obtained by ESI^--MS in scan mode. The entirety of results (HPLC-ICP-MS, HPLC-ESI-MS, ESI-TOF-MS, and HPLC-ESI-MS/MS) allows to assure that the amino group of the AA was oxidized to a nitro group probably by a catalytic action of the functionalities of the applied three soils in the following order LO < TL ~ AT. A correlation with the soils characteristics could not be established since the relative

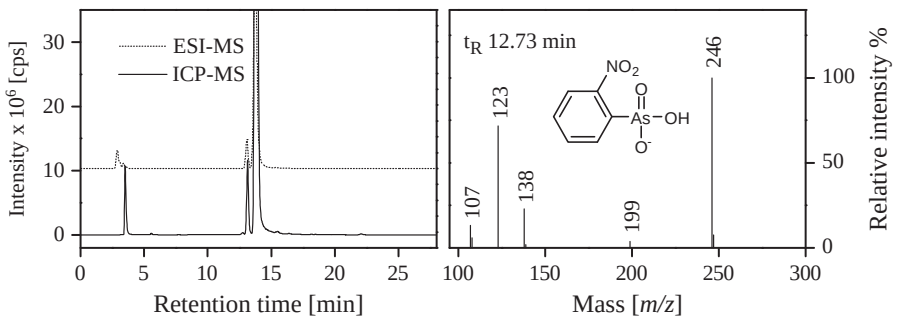

Fig. 2. HPLC-ESI-MS and ICP-MS chromatograms, and mass spectrum of the *o*-arsanilic acid solution in contact with the AT soil. The ESI-MS analysis was carried out in negative mode.

conversion degrees of AA were the same for the investigated soils (4.7% for LO, 4.8% for TL and 5.0% for AT).

Finally, the retention time (HPLC-ICP-MS/ESI-MS) of the proposed compound was compared with that obtained for the commercially available 2-nitrophenylarsonic acid (2NPA) used as standard substance (not shown). The retention time ($\pm$ 0.01 min) agreed exactly with that of the transformation product identified as nitrophenylarsonic acid. The mass spectra (not shown here) are also identical.

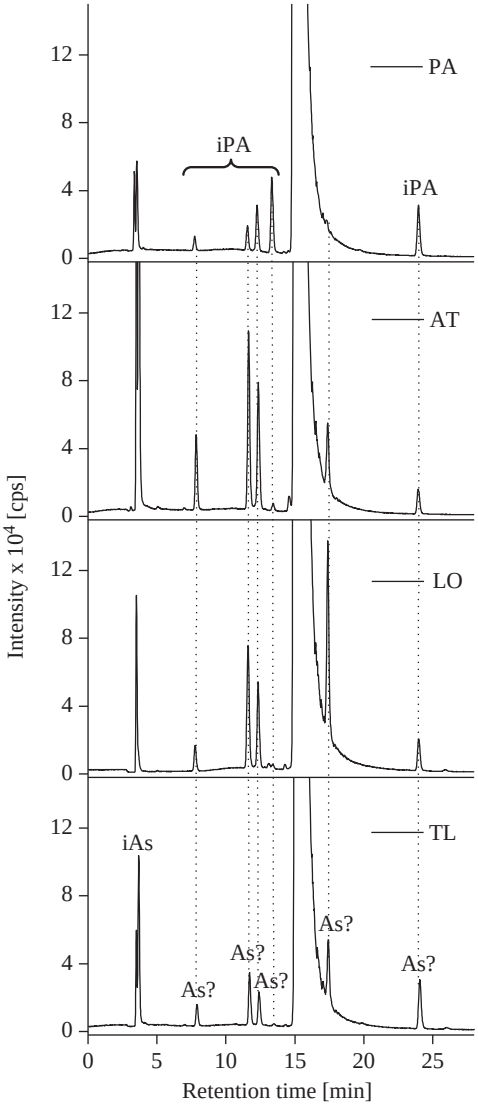

Fig. 3. HPLC-ICP-MS chromatograms of phenylarsonic acid (PA) treated with the *Acrisol* (AT), *Andosol* (LO) and *Tepetate* (TL) soils. (iAs) inorganic arsenic; (As?) unknown arsenic species and (iPA) impurities of PA.

3.2. Identification of the reaction products of phenylarsonic acid (PA)

HPLC-ICP-MS chromatograms of aqueous solutions of PA that were treated with the soils under investigation (AT, LO and TL) are shown in Fig. 3. Additionally a chromatogram of the initial PA solution was inserted in Fig. 3 to allow a comparison of the initial solution with the chromatograms of the reaction solutions of PA with the soils. The vertically dotted lines should facilitate a differentiation between the retention times of the primary impurities (iPA) in the initial solution and the products (As?) generated by reaction with the soils. An additional indicator for the interaction of PA with the soils can be found in the change of the peak intensity of the reaction products compared to the initial impurities (iPA), i. e. the promotion of the increase of the concentration of the impurity at the expense of the transformation of the PA.

When PA was in contact with the soil, the following effects could be observed: first, the content and the species of inorganic arsenic varied depending on the soil type; second, components of the initial solution of PA disappeared during the reaction time; and third, an additional peak at retention time 17.4 min arose probably corresponding to a transformation product of PA. Measured at ESI^+-MS mode the product proposed in Fig. 4 was identified with a molecular ion at *m/z* 201 ($[M+H]^+$). High resolution MS (ESI-TOF-MS) confirmed the theoretically calculated mass weight (*m/z* 200.9891) of the product with a signal with a value of *m/z* 200.9885 (spectrum not shown) and an error of -2.98 ppm. Additional HPLC-ESI-MS/MS investigations of precursor ion $[M+H]^+ = 201$ provided fragmentation ions at *m/z* 183 and 155 which agreed with those obtained in the scan mode by ESI^+-MS. With these results, it can be concluded that the PA underwent methylation as a result of the interaction with the soils in the following order: AT$\sim$TL$<$LO, at which LO is the soil with the highest amount of organic carbon. The methylphenylarsinic acid identified in our experiment as PA related product has been already detected in groundwater, rice and soil in areas contaminated by aromatic arsenicals [24–27].

3.3. Recognition of presumable degradation pathways

3.3.1. Degradation by visible light

The purpose of these studies was to compare degradation products of AA and PA obtained in soil slurries in comparison with irradiation studies to include/understand the degradation mechanism of phenylarsonic species. Preliminary tests showed that for example, irradiation of solutions of RO [12] with UV light

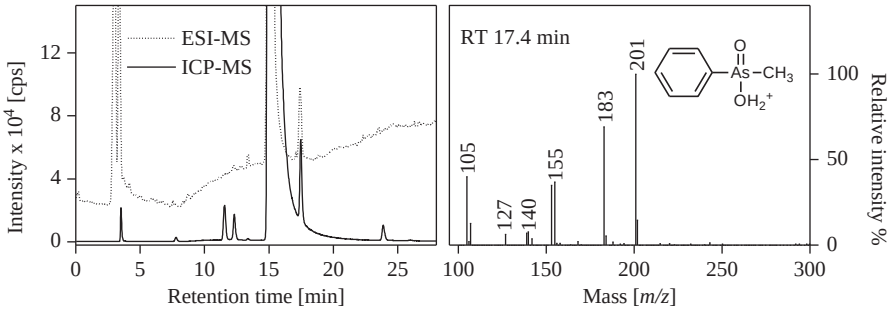

Fig. 4. HPLC-ESI-MS and ICP-MS chromatograms, and mass spectrum of the phenylarsonic acid solution in contact with the LO soil. The ESI-MS analysis was carried out in positive mode.

led to a fast transformation to inorganic arsenic (arsenate) without the formation of detectable organoarsenic intermediates.

Because of the above mentioned, we decided to use in these experiments only irradiation with visible light. Aqueous solutions of AA and PA were placed in glass vials to inhibit UV radiation and to expose them to unfiltered visible light for 6 and 24 h, respectively. The experiments with the AA showed that this one was degraded almost completely within 6 h of irradiation and that the photo-transformation to 2-nitrophenylarsonic acid with *m/z* 246 (Fig.2) was not observed during this process. Therefore, the transformation of AA should be the result of the interaction with soils. On the other hand, five decomposition products appeared in the PA solution. The following tendencies of the transformation out of PA described by the kinetic curves (Fig. 5) of the photolysis were observed: (i) after 6 h of irradiation 60% of the initial concentration of PA was decomposed to products comparable with that of the impurities in Fig. 3 between 5 and 14 min. They reached their maximum abundance at 6 h of irradiation; (ii) between 6 and 12 h a deceleration of the transformation process was observed and at 12 h a residue of 10% of PA remained in the reaction solution; and (iii) between 12 and 24 h the degradation products became transformed to nearly 100% of inorganic arsenic (see Fig. 5). The same trend was observed in other studies where irradiation was applied as well [28,29].

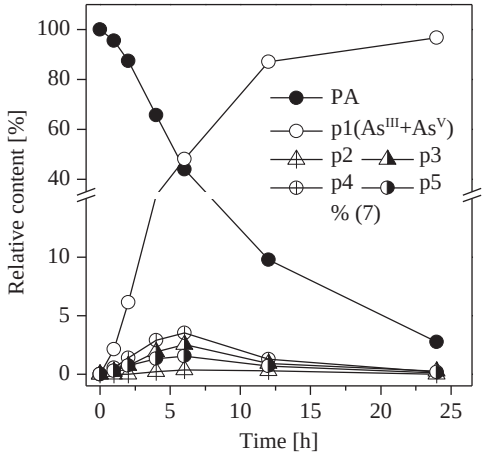

Fig. 5. Kinetic curves of the photolysis of PA. p1–p5 correspond to the peaks shown in the HPLC-ICP-MS chromatogram in figure 6.

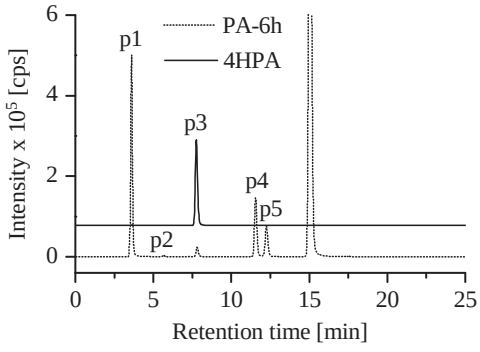

Fig. 6. HPLC-ICP-MS chromatograms of a PA solution irradiated with visible light during 6 h (dotted line) and of a solution of the 4-hydroxyphenylarsonic acid (continuous line).

Nevertheless, the methylphenylarsinic acid with *m/z* 201 (Fig. 4) was not formed confirming again that the products of the arsenic transformation were formed during a reduction process between the PA and the soils. The transformation process occurs via elimination of the hydroxyl group of the arsonic acid unit and the introduction of methyl group under anaerobic conditions [26] and mediated by microbial activity.

With complementary equipments and methods, the identification of the peaks observed within the 5 and 14 min could be managed. The compounds formed in the solution of PA after 6 h of irradiation were analyzed by means of HPLC-ICP-MS/ESI-MS, HPLC-ESI-MS/MS and ESI-TOF-MS working in negative ionization mode, and the results were compared were proved using 4-hydroxyphenylarsonic acid (4HPA) applied as a standard compound (Fig. 6). This compound corresponds to the peak with t_R 7.8 min and with a mass *m/z* 217. Nevertheless, three isomeric structures of 4HPA with *m/z* 217 exist (Fig. 7). On the basis of matching retention times, mass spectra and the correlation with the standard compound, the peaks at t_R 11.55 and 12.55 min turned out to be the 3-hydroxyphenylarsonic acid (3HPA) and the 2-hydroxyphenylarsonic acid (2HPA), respectively. In addition, at a retention time of 5.7 min a dihydroxyphenylarsonic compound (DHPA) with *m/z* 233 appeared in the same sample with low intensity, but not observed in the sample which was only in contact with soils (Fig. 3). Although these mono- and dihydroxylated phenylarsonic acids have been already identified as photoproducts of PA [25,26]. In this work they were observed as impurities of PA. Surprisingly, this result indicated that the use of irradiation on PA leads to the increase of the concentration of these impurities but not to the formation of new photoproducts.

4. Conclusions

A set of organoarsenicals were identified in phenylarsonic acid (PA) and *o*-arsanilic acid (AA) solutions in contact with soil of volcanic origin and deionized water in batch systems. The transformation products were identified with element selective (ICP-MS) as well as molecular selective (ESI-MS) detection after their HPLC separation. The identification of the main transformation

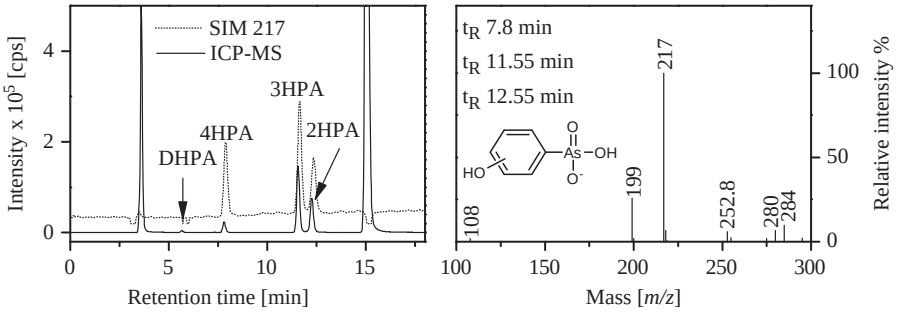

Fig. 7. HPLC-ICP-MS/ESI-MS chromatograms of a solution of PA irradiated with visible light during 6 h and ESI$^-$-MS spectrum of the peaks at 7.8, 11.55 and 12.55 min. ESI-MS as *single ion monitoring* (SIM) in negative mode.

products by means of ESI-MS, ESI-MS/MS and ESI-TOF-MS showed the occurrence of nitrophenylarsonic acid in the AA solution and of methylphenylarsinic acid in the PA solution both in contact with soils. The information obtained on the accurate mass values (ESI-TOF-MS), with very low mass errors (<5 ppm), of the transformation products and their product ions (ESI-MS/MS), evidently support the information obtained by nominal mass measurements (ESI-qMS).

Using irradiation of PA solution with visible light, different compounds observed as impurities of PA were detected with remarkable increase in intensity and therefore could be identified as 4-hydroxyphenylarsonic acid, 3-hydroxyphenylarsonic acid and 2-hydroxyphenylarsonic acid. Additionally, a dihydroxyphenylarsonic compound was identified as impurity of PA as well.

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