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Ion-exchange separation of eight arsenic compounds by high-performance liquid chromatography–UV decomposition–hydride generation–atomic fluorescence spectrometry and stability tests for food treatment procedures

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Abstract

A novel separation for cationic arsenic compounds on a polymer-based cation-exchange column was developed using an ion-pairing reagent (3-carboxy-4-hydroxybenzenesulphonic acid) in the mobile phase. An existing anion-exchange separation was used for anionic arsenic compounds. Combining both separation techniques, eight environmentally important arsenic compounds can be determined using on-line decomposition in a UV reactor prior to hydride generation (HG) and atomic fluorescence spectrometry (AFS). The method was applied for testing the stability of arsenic compounds (in aqueous media) related to food treatment procedures. Boiling and microwave treatment gave no degradation, whereas γ-irradiation and dry heating resulted in partial decomposition of several arsenic compounds. No health hazards are to be expected when these data are extrapolated to commercial or domestic food treatment procedures. © 1997 Elsevier Science B.V.

Keywords: Detection, LC; Food analysis; Arsenic compounds; Arsenobetaine

1. Introduction

Arsenic is a ubiquitous element with an average concentration in the earth's crust of 20 mg kg^{-1}; in natural waters its concentration ranges from 0.2 to 40 ng ml^{-1} [1,2]. The most abundant arsenic species in natural waters is As(V), after As(III) the most toxic arsenic species. Some living organisms in marine systems are able to accumulate and efficiently metabolise arsenic, in general leading to detoxification. Marine animals contain non-toxic arsenobetaine (AB) as the major arsenic species and minor amounts of the tetramethylarsonium ion (TETRA) and traces of trimethylarsineoxide (TMAO), arsenocholine (AC), dimethylarsinic acid (DMAA), As(III) and As(V). In some marine animals arsenosugars were also identified, compounds which are the predominant arsenic species in marine algae. Algae also contain minor amounts of As(V) and traces of DMAA and monomethylarsonic acid (MMAA). The highest arsenic concentrations (3–50 mg kg^{-1}, mainly AB) are found in crustaceans (shrimps, crabs, etc.), followed by molluscs and fish [3]. In terrestrial systems a variety of arsenic compounds was found in higher fungi (mushrooms) [4,5]. AB is the major species in most orders studied, and there appears to be a relationship between taxonomy and arsenic compounds present, the more primitive fungi having predominantly more inorganic and fewer methylated species.

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Marine animals and to a lesser extent mushrooms are an important source of arsenic in the human diet. Although ingestion involves no toxic effects because of the predominance of AB, food treatment procedures might partly decompose AB to more toxic compounds. According to our knowledge, no data are available on the stability of arsenic species in relation to food treatment procedures. Preliminary experiments [6] showed that γ-irradiation might partly decompose arsenic compounds. As γ-irradiation may be used for preservation (sterilisation and prolongation of shelf-life) of foods, also in the case of seafood and mushrooms [7,8], study on the effect of food treatment procedures on the stability of arsenic compounds seems justified.

In order to study the decomposition of arsenic compounds, high-resolution speciation techniques have to be used. For arsenic this means separation in the HPLC mode combined with detection with an element-specific detector. Since the arsenic species mentioned above are anionic, cationic and/or neutral, depending on pH, complete separation of all eight arsenic species (As(III), As(V), MMAA, DMAA, AB, AC, TETRA and TMAO) on a single column is difficult to achieve. Ion-pair reversed-phase chromatography has been applied with some success for the separation of up to seven arsenic species [9,10]. However, a combination of anion- and cation-exchange materials seems most promising for complete resolution of all eight arsenic compounds [11]. Mostly, various modes of atomic absorption spectrometry or inductively coupled plasma mass spectrometry are used for detection. Recently atomic fluorescence spectrometry has been applied as a very sensitive means of detection with either on-line microwave digestion [9] or UV digestion [12], prior to hydride generation.

In this work HPLC–UV–HG–AFS with separation of eight arsenic compounds on a combination of anion- and cation-exchange columns was performed with respect to the compatibility of the mobile phase with on-line UV digestion and hydride generation. An anion-exchange separation was applied for determination of anionic arsenic compounds [12] and a cation-exchange separation method was developed for determination of cationic arsenic compounds on a polymer-based resin using an ion-pairing reagent. As only anionic arsenic compounds form hydrides, a sensible use of the UV photoreactor (on/off) allowed us to prevent chromatographic overlap with cationic arsenic compounds on the anion-exchange column [13]. The method was applied to investigate the stability of arsenic species in relation to γ-irradiation and several heat treatments (boiling, dry heating and microwave heating).

2. Experimental

2.1. Materials

All chemicals were of analytical grade. Millipore (Milford, MA, USA) Milli-Q Plus water (18.2 MΩ cm) was used for all solution preparations. As_2O_3 and As_2O_5 were purchased from Merck (Darmstadt, Germany) and MMAA, DMAA, AB-bromide, TMAO, AC-bromide and TETRA-iodide were gifts from Professor K.J. Irgolic (Karl-Franzens University, Graz, Austria). Stock solutions of the arsenic compounds containing about 1000 mg l^{-1} arsenic (the exact concentration of arsenic in the stock solutions was determined by instrumental neutron activation analysis (INAA)) were prepared in water and kept at 4°C. Appropriate dilution of the stock solutions with water yielded working solutions with arsenic concentrations of 10–100 ng ml^{-1}; these solutions were prepared fresh daily. An overview of the properties of the arsenic compounds is given in Table 1.

2.2. Speciation apparatus

In Fig. 1 an outline of the HPLC–UV–HG–AFS system is shown and details of the system are given below. Experimental details and optimal operating conditions are given below.

2.2.1. HPLC separation

Arsenic compounds were separated using an LKB Bromma 2150 HPLC-pump (Sweden) fitted with a Hamilton PRP-X100 anion-exchange column (250× 4.1 mm; mobile phase, KH_2PO_4, 15 mmol l^{-1}, pH 6.1 (NH_4OH), 1 ml min^{-1}) or a Hamilton PRP-X200 cation-exchange column (250×4.1 mm; mobile phase, 3-carboxy-4-hydroxybenzenesulphonic

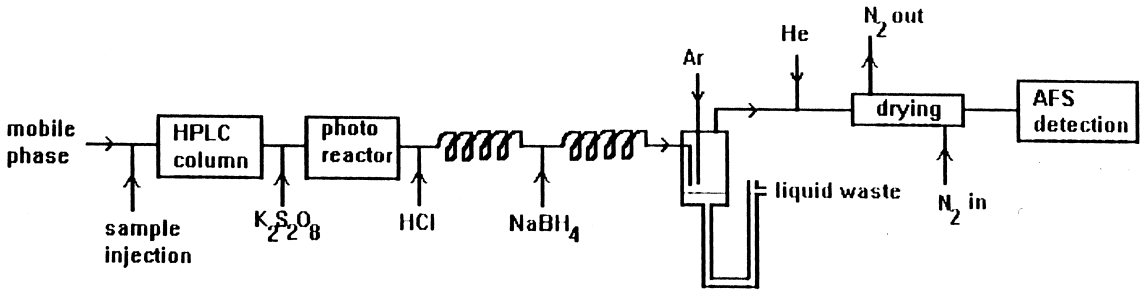

Fig. 1. Schematic diagram of the HPLC–UV–HG–AFS system for arsenic speciation including HPLC separation, UV decomposition, hydride generation (HG) and AFS detection of arsenic compounds.

acid, 5 mmol l^{-1}, pH 1.90 (HCl), 1 ml min^{-1}); guard columns were of the same material as the analytical columns. Samples were injected via a Rheodyne 7125 injector (Rheodyne, Cotati, CA, USA) with a 100-μl sample loop.

2.2.2. Photochemical oxidation

The HPLC effluent was delivered to a PTFE T-cross via polyether ether ketone (PEEK) tubing (30 cm×0.05 cm I.D.) and mixed with potassium persulphate solution (4% (w/v) in 3% (w/v) NaOH, 1.35 ml min^{-1}) added by a peristaltic pump. Subsequent photochemical decomposition took place in a custom-made UV-reactor (Kobis UVR-010, Ljubljana, Slovenia): PTFE tubing, 3.1 m×0.5 mm I.D., coiled around an 8-W 254-nm UV-lamp (Camag).

2.2.3. Hydride generation

The decomposed compounds in the effluent were mixed and reacted with hydrochloric acid (4.4 mmol l^{-1}, 2.9 ml min^{-1}) and sodium borohydride (1.5% (w/v) in 0.1% (w/v) NaOH, 2.9 ml min^{-1}) in a standard PTFE mixing coil assembly (PS Analytical, Orpington, UK). Both reagents were added by a peristaltic pump. The gas–liquid mixture was delivered to an 'A' type gas–liquid separator (PS Analytical) via PTFE tubing (95 cm×1 mm I.D.). The arsines and hydrogen evolved were swept from the separator with a flow of argon (350 ml min^{-1}).

2.2.4. AFS detection

For optimal detection stability helium was added (80 ml min^{-1}) to the outflowing gases of the gas–liquid separator prior to drying in a 'Perma-Pure' mini-dryer (Perma Pure Products, Farmingdale, USA). After drying, the arsines entered the atomic fluorescence spectrometer (model Excalibur, PS Analytical) and were atomized in a hydrogen/air flame aligned in the lightpath of a boosted As hollow cathode lamp (Superlamp P803S Photron, Australia; primary current, 27.5 mA; boost current, 35 mA). Atomic fluorescence signals were recorded with a strip-chart recorder. All data are based on measurement of peak heights.

2.3. Separation methods

For HPLC separation on an anion-exchange column previously reported conditions [12] were used giving baseline separation of As(III), DMAA, MMAA and As(V). For HPLC separation on the cation-exchange column conditions were tested with regard to resolution, sensitivity and compatibility with UV digestion and hydride generation. To this end several mobile phases (pyridine/formic acid, formic acid, citric acid, pyridine/citric acid, phosphate buffer, hydrochloric acid/3-carboxy-4-hydroxybenzenesulphonic acid) at different concentrations and pH values were applied.

2.4. Procedures for stability testing of arsenic compounds

2.4.1. γ-Irradiation

Amounts of 5.9–15.1 mg of MMAA, DMAA and AB were dissolved individually in 2 ml of water in a polyethene vial (3.5 ml). After sealing, the vials were irradiated by a ^{60}Co-γ source (Rudjer Bošković Institute, Zagreb, Croatia). Duplicate samples were

subjected to a dose of either 10 or 100 kGy. Although the latter dose is unrealistically high (doses up to 5 kGy are normally used in food sterilization procedures), it will amplify the degradation effect. After irradiation the samples were frozen (−18°C) until analysis. Defrosted samples were diluted ca. 2000-fold with water prior to analysis.

2.4.2. Microwave treatment

Aqueous standards (MMAA, DMAA, AB and TETRA) of ca. 100 μg l^{-1} (50 ml) were placed in glass beakers individually and subjected to 300 W of microwave power for 120 min. During heating the water evaporated completely. The residues were taken up in 50 ml of water prior to analysis.

2.4.3. Boiling

Aqueous standards (MMAA, DMAA, AB and TETRA) of ca. 100 μg l^{-1} (50 ml) were placed in glass beakers individually and boiled gently on a hot plate for 100 min. During boiling the volume was kept constant by addition of water. Samples were analysed directly after cooling to room temperature.

2.4.4. Dry heating

Aqueous standards (MMAA, DMAA, AB and TETRA) of ca. 100 μg l^{-1} (50 ml) were placed in glass beakers individually. The water in duplicate samples was evaporated in an oven and the dry residues were further heated for either 30 min or 24 h at 160°C. After cooling the residues were taken up in 50 ml of water prior to analysis.

3. Results and discussion

3.1. Separation

A typical chromatogram for separation of the anionic arsenic compounds on an anion-exchange column is given in Fig. 2. Baseline separation of all four compounds is obtained. Cationic arsenic compounds would elute in the void volume; i.e., with similar retention times as As(III) [12], since they are not retained on an anion-exchange column. However, without photochemical oxidation, they will be invisible as cationic arsenic compounds do not form hydrides (an exception is TMAO which forms tri-

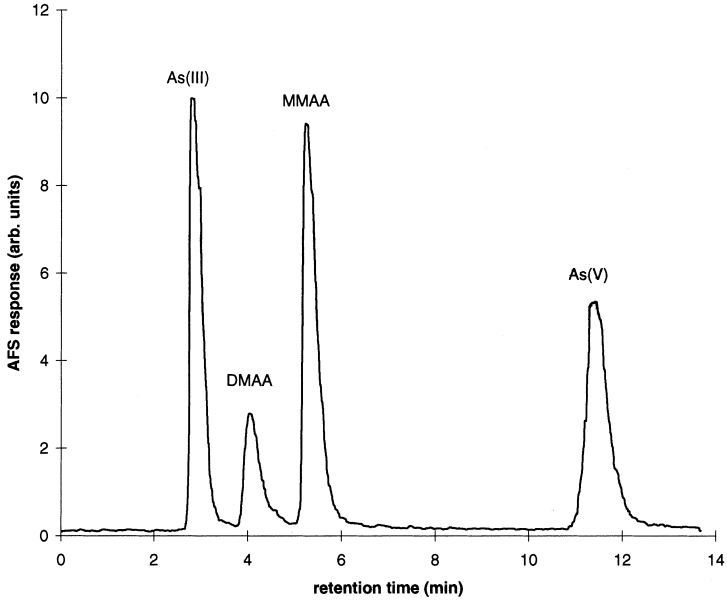

Fig. 2. Anion-exchange separation of 100 ng ml^{-1} As(III), 100 ng ml^{-1} As(V), 107 ng ml^{-1} MMAA and 107 ng ml^{-1} DMAA. Experimental conditions: Hamilton PRP-X100 anion-exchange column; mobile phase, phosphate buffer (15 mmol l^{-1}, pH 6.1); injection volume, 100 μl; flow-rate, 1 ml min^{-1}; without photochemical oxidation; void volume, 2.5 ml.

methylarsine, but to a negligible extent). Unlike anionic arsenic compounds they have to be decomposed prior to hydride generation. To be able to separate the cationic arsenic compounds cation-exchange chromatography was developed. Overlap with anionic arsenic compounds had to be prevented as photochemical oxidation had to be performed for the detection of cationic arsenic compounds.

AB is a zwitterion above pH 2.18 (Table 1), and has a positive charge (cationic character) under more acidic conditions. In the pH range studied (1–5), the positive charge will always be lower than for the other three cationic species (Table 1) and, thus, the retention time on a cation-exchange column should be the shortest. AC and TETRA are positively charged, independent of pH, which means that cation-exchange separation on a polymer-based column can only be achieved by non-ionic (hydrophobic, steric, etc.) interactions with the column material. Theoretically this means that separation is also possible due to differences in size and hydrophobicity. TMAO has a different three-dimensional structure than the other cationic compounds in which the arsenic atom is surrounded by four carbon atoms. In TMAO the arsenic atom is surrounded by three carbon atoms and one oxygen atom. Thus, a different retention behaviour might be expected; e.g., a smaller hydrophobic interaction but more cation-exchange interaction due to lower shielding of the arsenic atom.

Larsen et al. [11] were able to separate the four cationic compounds (AB, AC, TETRA and TMAO) on silica-based columns using pyridine/formic acid as a mobile phase. In our system the same mobile phase consisting of 0.02 mol l^{-1} pyridine (pH adjusted to 2.65 with formic acid) gave no response for the cationic compounds but the anionic compounds (As(III), As(V), MMAA and DMAA) gave a normal response. This suggests that the hydride generation itself was not affected, but the decomposition efficiency in the UV reactor due to the presence of UV-light-absorbing components in the mobile phase. By testing the mobile-phase components individually it was shown that formic acid is responsible for this effect but for so far unknown reasons. In a trial experiment to circumvent these problems, citric acid was used instead of formic acid (mobile phase: 0.020 mol l^{-1} pyridine, pH adjusted to 2.65 with citric acid). In this instance the response was not impaired but separation of the cationic compounds on the styrene–divinylbenzene column Hamilton PRP-X200 gave poor resolution; only AB was separated from the coeluting compounds AC, TETRA and TMAO. Citric acid on its own (0.05 mol l^{-1}, pH adjusted with ammonia to 2.65–3.37) gave better separation characteristics, as AB and TETRA could be separated from the coeluting compounds TMAO and AC (Fig. 3).

If we assume the pH to be the only variable affecting the separation, then a lower pH (at constant ionic strength) should result in better retention of AB and TMAO as more cationic character is induced and unchanged retention of AC and TETRA as their charge is independent of pH (Table 1). As shown in Fig. 4, all four compounds have the same retention time correlation with pH (parallel curves) what is not expected. This makes it obvious that more processes play a role in the separation procedure, which is

Table 1
Arsenic compounds and their pK_a values [14,15]; for abbreviations trivial names in use in the scientific literature are given; formulas represent the highest protonated species occurring around the lowest pK_a value

Compound	Abbreviation	Formula	pK_a
Anionic			
Arsenous acid	As(III)	H_3AsO_3	9.2
Arsenic acid	As(V)	H_3AsO_4	2.3, 6.7, 11.6
Monomethylarsonic acid	MMAA	$CH_3AsO(OH)_2$	3.6, 8.2
Dimethylarsinic acid	DMAA	$(CH_3)_2AsO(OH)$	6.3
Cationic			
Arsenobetaine	AB	$(CH_3)_3As^+CH_2COOH$	2.18
Arsenocholine	AC	$(CH_3)_3As^+CH_2CH_2OH$	None
Tetramethylarsonium ion	TETRA	$(CH_3)_4As^+$	None
Trimethylarsine oxide	TMAO	$(CH_3)_3As^+OH$	3.6

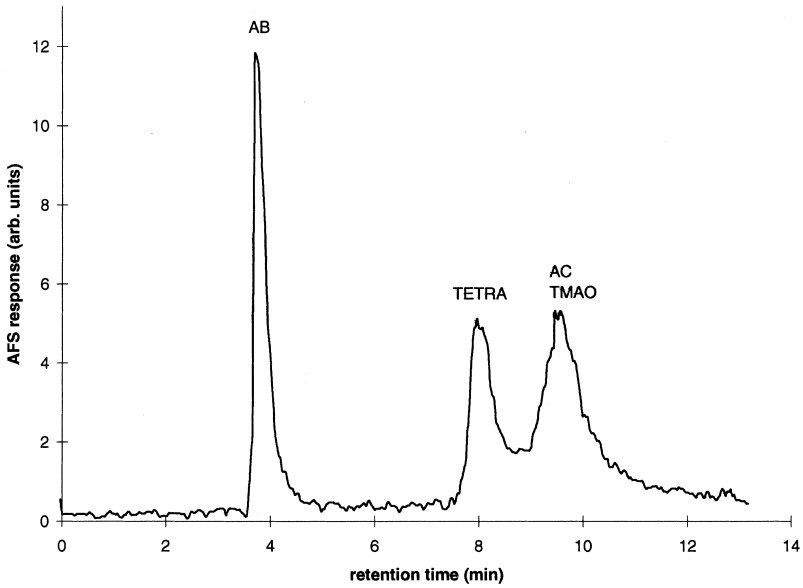

Fig. 3. Cation-exchange separation of AB, TETRA, TMAO and AC (100 ng ml^{-1} each). Experimental conditions: Hamilton PRP-X200 cation-exchange column; mobile phase, citric acid (50 mmol l^{-1}, pH 3.4); injection volume, 100 μl; flow-rate, 1 ml min^{-1}; with photochemical oxidation; void volume, 2.9 ml.

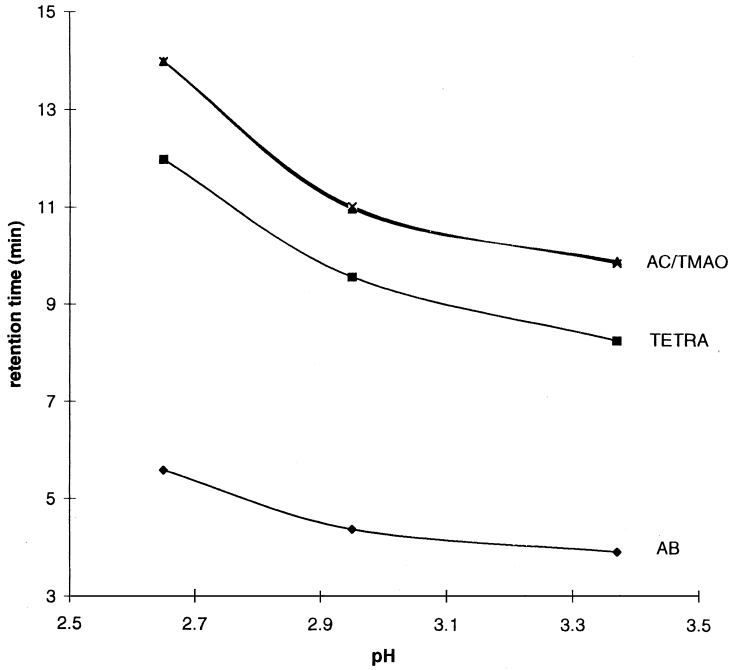

Fig. 4. Retention times of AB, TETRA, TMAO and AC on a cation-exchange column as a function of pH of the mobile phase (citric acid).

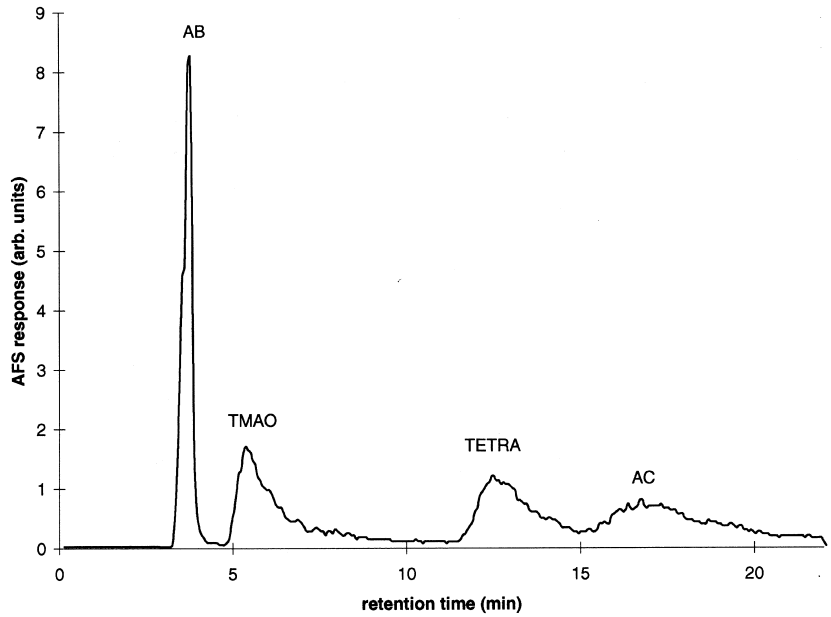

Fig. 5. Cation-exchange separation of AB, TETRA, TMAO and AC (100 ng ml^{-1} each). Experimental conditions: Hamilton PRP-X200 cation-exchange column; mobile phase, phosphate buffer (30 mmol l^{-1}, pH 5.0); injection volume, 100 μl; flow-rate, 1 ml min^{-1}; with photochemical oxidation; void volume, 3.2 ml.

emphasised in Fig. 5 where at pH 5.0 (mobile phase: 0.03 mol l^{-1} phosphate buffer) the expected sharp AB peak elutes in the void volume, followed by the very broad peaks of the other cationic arsenic compounds of which TMAO, on the basis of its pK_a value, should elute in the void volume as well. Although complete separation is obtained in this way, AB elutes with the anionic compounds. Many more parameters were varied but none of them resulted in complete separation of the cationic compounds without overlapping with the anionic ones at the same time. To further promote separation the hydrophobic character of the column was enhanced by adding an ion-pairing reagent; viz, 3-carboxy-4-benzenesulphonic acid, to the mobile phase. This reagent has pK_a values of -0.75, 2.5 and 11.8 [10] and might help to resolve TMAO and AC.

As can be seen from Fig. 6, the addition of this ion-paring reagent to the mobile phase increased the retention times of AB, TETRA and AC, while TMAO showed a different trend which makes it possible to separate the four cations using 5–10 mmol l^{-1} of 3-carboxy-4-benzenesulphonic acid. Although no baseline separation was achieved, with deconvolution software it was possible to calculate peak heights and areas. As illustrated in Fig. 7, separation is accomplished without interference from anionic arsenic compounds. The ion-pairing reagent does not influence the anionic signals but cationic signals are lowered, probably due to incomplete decomposition in the UV reactor, since the mobile phase partially absorbs the UV light (254 nm) used for decomposition. The higher the ion-pairing reagent concentration, the lower the cationic signals; an optimum 3-carboxy-4-benzenesulphonic acid concentration of 5 mmol l^{-1} was chosen for all further experiments.

3.2. Stability testing

The chemical stability of AB is very high, even under extreme conditions (wet decomposition with concentrated oxidising acids) [16]. Although these conditions will never be met in normal food treatment procedures, partial decomposition as observed in γ-irradiation experiments [6] indicated that certain

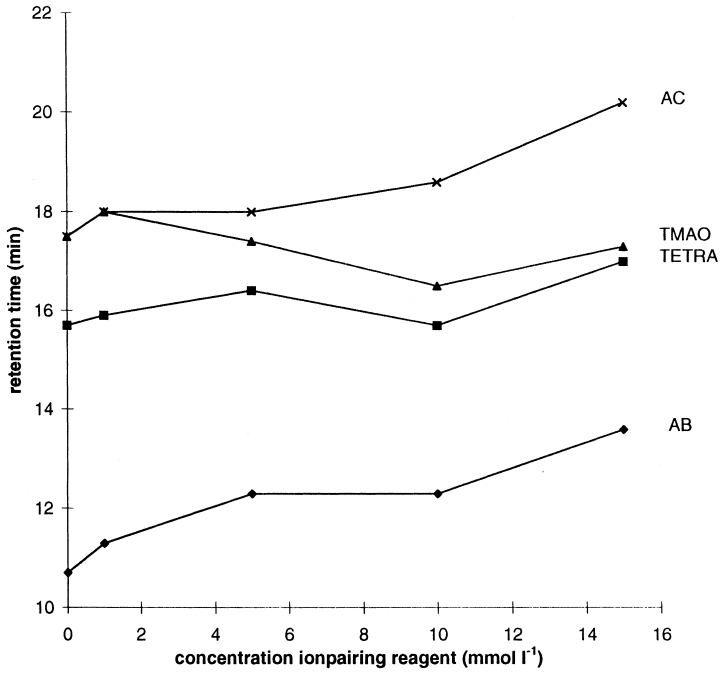

Fig. 6. Retention times of AB, TETRA, TMAO and AC on a cation-exchange column as a function of the concentration of ion-pairing reagent in the mobile phase (10 mmol l^{-1} HCl).

procedures might result in health hazards due to decomposition of, for example, non-toxic AB into toxic arsenic degradation products. The same might be true for normal domestic food treatment procedures with heating (microwave treatment, boiling and dry heating), but to our knowledge no data are available for the effects of such procedures on the stability of arsenic compounds. To this end the stability was investigated using both γ-irradiation and heat treatment procedures. In order to see the effect of the procedures on the formation of degradation products, unrational food treatment conditions (high γ dose and long heating time) were also applied. As the stability is related to arsenic compounds in seafoods and mushrooms, only a selection of the most abundant compounds was investigated.

From Table 2 it can be seen that γ-irradiation of aqueous arsenic-containing solutions results in partial decomposition of all compounds (AB, MMAA and DMAA) studied, especially in the case of a high γ dose (100 kGy). Under these conditions ca. 30% of AB and MMAA and ca. 15% of DMAA were converted into other and more toxic arsenic compounds. Demethylation took place for all compounds with additional conversion of AB to TMAO (17%) and TETRA (1.5%). The effect of a low γ dose (10 kGy) is much less pronounced, yielding a maximum conversion of 5% for AB. In commercially applied γ-irradiations of food the γ dose is usually under 5 kGy [7,8], so that health hazards are not to be expected if we assume that in biological matrices the arsenic compounds behave similarly under such treatments. This is a fair assumption since most biological matrices consist, for a substantial part, of water which is the main 'supplier' of radicals in γ-irradiation [17].

Under boiling and microwave treatment, aqueous solutions of MMAA, DMAA, AB and TETRA remained stable. In both cases temperatures never exceeded 100°C. From Table 3 it follows that even short (30 min) heating at 160°C resulted in 6–10% decomposition (MMAA, DMAA and AB), whereas no degradation was observed for TETRA. Heating for a longer time (24 h) resulted in ca. 80% decomposition of AB and ca. 50% decomposition of MMAA; DMAA and TETRA are partly decomposed

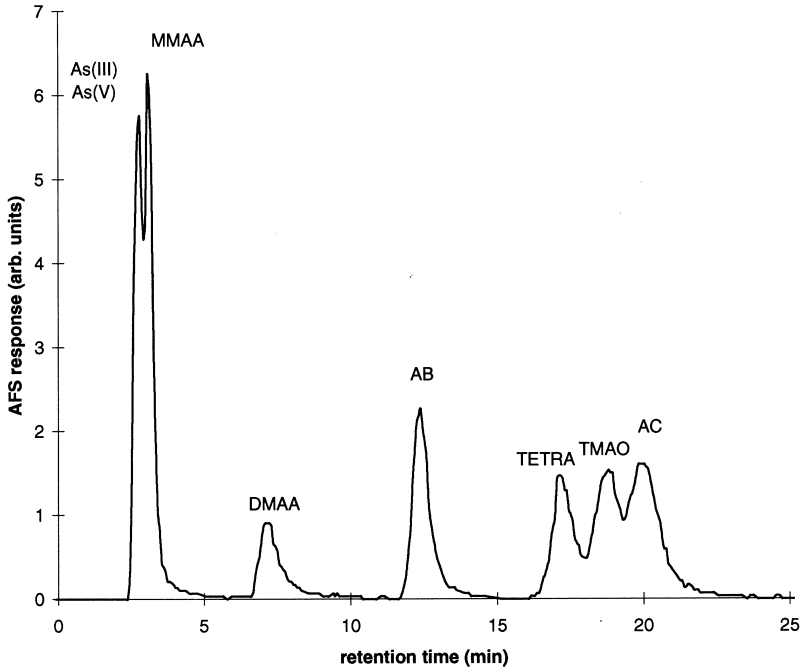

Fig. 7. Cation-exchange separation of As(III), As(V), MMAA, DMAA AB, TETRA, TMAO and AC (100 ng ml^{-1} each, except MMAA and DMAA, 107 ng ml^{-1}). Experimental conditions: Hamilton PRP-X200 cation-exchange column; mobile phase, 3-carboxy-4-hydroxybenzenesulphonic acid (5 mmol l^{-1}, pH 1.90); injection volume, 100 μl; flow-rate, 1 ml min^{-1}; with photochemical oxidation; void volume, 2.5 ml.

to volatile degradation products as the sum of species is lower than 100%. The high temperatures experimentally applied (160°C) are rarely obtained inside the food, even during grilling and frying, because the amount of water present in food prevents in situ food temperatures rising much above 100°C [18]. Although the outside food temperature might resemble the food treatment procedure temperature, the fact that both surface/volume ratio and inside temperature are low, an increased health hazard due to decomposition of arsenic compounds is improbable.

Table 2
Degradation products resulting from γ-irradiation of aqueous solutions of MMAA, DMAA and AB; averages and standard deviations of triplicate determinations are given

Compound irradiated (mg ml^{-1})	Irradiation dose (kGy)	Degradation products (% of sum of species)						
		As(III)	As(V)	MMAA	DMAA	AB	TMAO	TETRA
AB (0.9)	10	nd	nd	nd	nd	95.0±6.4	5.0±0.4	nd
MMAA (4.0)		0.5±0.1	1.0±0.1	98.5±6.3	nd	nd	nd	nd
DMAA (3.6)		0.7±0.1	0.3±0.1	0.3±0.1	98.7±7.2	nd	nd	nd
AB (1.3)	100	0.9±0.1	6.9±0.5	0.5±0.1	2.9±0.2	69.8±4.7	17.5±1.2	1.5±0.2
MMAA (2.6)		8.6±0.6	19.3±1.4	71.9±5.9	nd	nd	nd	nd
DMAA (2.2)		3.8±0.2	7.3±0.5	3.7±0.4	85.1±5.5	nd	nd	nd

nd, not detectable.

Table 3
Degradation products resulting from heat treatment of MMAA, DMAA, AB and TETRA at 160°C for different heating times; averages and standard deviations of triplicate determinations are given

Compound treated	Heating time	Degradation product (% of the original compound treated)						
		As(III)	As(V)	MMAA	DMAA	AB	TMAO	TETRA
MMAA	30 min	9±1	nd	91±4	nd	nd	nd	nd
DMAA		nd	nd	6±3	94±6	nd	nd	nd
AB		nd	nd	nd	nd	90±3	10±2	nd
TETRA		nd	nd	nd	nd	nd	nd	100±4
MMAA	24 h	39±1	9±2	52±2	nd	nd	nd	nd
DMAA		3±1	nd	5±1	44±1	nd	nd	nd
AB		nd	nd	nd	nd	21±1	11±1	68±3
TETRA		nd	nd	nd	nd	nd	nd	78±3

nd, not detectable.

4. Conclusions

Separation of eight arsenic compounds was achieved using an anion- and a cation-exchange column for anionic and cationic arsenic compounds, respectively. Baseline separation of anionic compounds was obtained using standard procedures; for the cationic compounds the separation conditions were tested for compatibility with the chemical interface (UV–HG). Separation of cations under standard conditions yielded poor resolution, in spite of the theoretical suitability of the mobile phase for separation. More interactions (hydrophobic, steric, etc.) of the cations on the column were observed, impairing the cation-exchange behaviour. However, these interactions, especially the hydrophobic interactions, could be used to extend the separation characteristics of the polymer-based column by addition of an ion-pairing reagent (3-carboxy-4-benzenesulphonic acid). In this instance separation of all four cations was achieved without overlapping with the anions.

Applying the optimised separation method, the stability of several arsenic compounds in food treatment procedures (γ-irradiation and heat treatments) was studied. Special emphasis was paid to compounds which are known to be present in seafood and mushrooms. In general no significant decomposition can be anticipated by extrapolating the results found to food treatment procedures, although decomposition of some compounds was found at high γ doses and long-term heating at high temperature (160°C).

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