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Filterless pre-concentration by co-precipitation by formation of crystalline precipitate in the analysis of barium by FIA-FAES

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A novel method based on flow injection analysis (FIA) and flame atomic emission spectrometry (FAES) is presented. It was developed for direct determination of barium in drinking water, in natural water, in digested samples of bone and liver, in saline water and in a standard reference material (NIST SRM 1640). It was found that digestion of bone by an incineration procedure was required, in order to extract most of the barium. In the FIA manifold, barium was pre-concentrated by co-precipitation with lead chromate leading to a crystalline deposit that adhered well to the inner walls of a nylon knotted reactor (KR). The method documents a novel example of formation of a crystalline compound during the pre-concentration step. The method comprises filterless pre-concentration by co-precipitation that proceeds successfully in a FIA system. An enrichment factor (EF) of 24 was achieved under normal working conditions at a sampling frequency of 50 h^{-1}. The detection limit (LOD, 3σ) was determined as 0.8 μg L^{-1} and species of iron(II) and iron(III) constituted the main species of interference.

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is most frequently applied to the analysis of barium at the ultra-trace level.[1–3] However, direct determination of barium by ICP-MS in saline matrices in some cases may be jeopardised by the presence of chloride, sodium, calcium or similar abundant species that may initiate corrosion of the detector. Since barium is found everywhere in the environment at trace level concentrations, it is important to evaluate methods that allow precise and rapid determination. In samples of human urine and in serum, barium is found in quantities of μg L^{-1}.[1,4] Because barium accompanies magnesium and calcium in many matrices, it might be expected that the element possess physiological properties. However, despite the fact that all barium compounds are considered toxic, except the sulfate, relatively large amounts are allowed in drinking water—up to 2 mg L^{-1}.[5]

A protocol was developed, which enables barium to be pre-concentrated by co-precipitation with lead chromate. It is a demonstration of on-line pre-concentration of barium without filtering where the co-precipitation agent results in the formation of a crystalline matter during analysis, as opposed to the more frequent formation of gelatinous precipitates.[6,7] Tentatively, this opens new gateways to co-precipitation schemes where the method is applied to other crystalline systems. The mechanism of co-precipitation is supported by the principle of Paneth–Fajans–Hahn and by the Pauling observation. Thus, barium is co-precipitated by entering crystallographic sites of lead in the chromate and the precipitate adsorbs well to a hydrophilic knotted reactor (KR) of nylon. The barium was collected in the KR of a flow-injection manifold and subsequently dissolved by hydrochloric acid followed by flame atomic emission spectrometry (FAES) detection. The protocol provided a factor of 24 improvement of the signal at a sampling rate of 50 h^{-1} and with a detection limit (3σ) of 0.8 μg L^{-1}. The influence of several interfering species was studied and the method was applied to samples of domestic water, saline water, liver, bone, hair and validated on a certified reference material (NIST SRM 1640).

Experimental

Instrumentation

A PerkinElmer Analyst 2100 atomic emission spectrometer equipped with a FIA-pre-concentration manifold was employed. The elements were analysed using their most sensitive and selective wavelengths, as recommended by the manufacturer using a nitrous oxide–acetylene flame: Mg (285.2 nm), Ba (553.6 nm), Sr (460.7 nm), Zn (213.9 nm), Fe (403.3 nm) and Cu (327.4 nm). The slit width was 0.2 nm in all experiments. A solution of 0.2–0.5% KCl (Merck 4935) was applied as modifier during the analysis of barium.

The original design of a FIA manifold, as proposed by Fang *et al.* and by Eidecker and Jachworth,[8,9] was applied to the pre-concentration protocol. A schematic diagram of the FIA manifold in both load-mode and injection-mode is shown in Fig. 1. In the injection mode, the sample was mixed in the mixing coil (MC) with co-precipitant no. 1 (lead ions). Subsequently, the mixture meets co-precipitation reagent no. 2 (buffer + chromate) in the KR where the pre-concentration proceeds within a specified period of time. Upon injection, pump no. 2 was deactivated and the carrier (HCl) was introduced into KR by pump no. 1, which caused rapid dissolution of the pre-concentrate ($Ba/PbCrO_4$) (Fig. 1). Automatic operation of the FIA manifold was accomplished by a FIAS 200 box (Perkin Elmer). The tubes were 0.5 mm (id) Microline except for the knotted reactor where 0.58 mm (id) Portex tubing was applied. By using optimisation procedures such as factor analysis and Taguchi statistics, an optimum design was obtained for the specific protocol of barium analysis. The optimum conditions of analysis were obtained at the conditions shown in Table 1.

Reagents

The standards were prepared from certified-stock solutions with concentrations of 1000 mg L^{-1} and diluted by the blank solution, as follows: magnesium (Merck 1.19778), calcium (Merck 1.19788), strontium (Merck 19799), barium (Merck 1.19774). The sodium and magnesium samples more

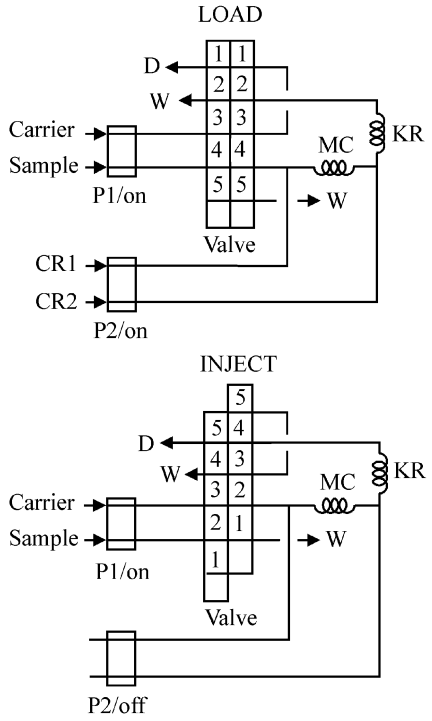

Fig. 1 Schematic diagram of the FIA manifold that was equipped with two pumps (P1 and P2), an injection valve (Valve), a mixing coil (MC) and a knotted reactor (KR). In the load mode (LOAD) both pumps are operated thus merging in the mixing coil (MC) the flow of sample with the flow of co-precipitating reagent no.1 (CR1, lead ions). The mixing was followed by pre-concentration with chromate (co-precipitation reagent no. 2, CR2) in the knotted reactor (KR). In the inject mode (INJECT), the co-precipitate retained by the KR was dissolved by the carrier (HCl) and analysed by FAES.

concentrated than 100 mg L^{-1} were prepared from NaCl (p.a. Merck) and $MgSO_4.6H_2O$ (Riedel de Häen 31420), respectively. The lead solutions (co-precipitation reagent 1; CR1, Fig. 1) were prepared from $Pb(NO_3)_2$ (The British Drug Houses 0307980), the iron solutions from $FeCl_3.6H_2O$ (p.a. Merck 3943)/$FeCl_2.4H_2O$ (p.a. Merck 3861) and the zinc solutions from $ZnCl_2.2H_2O$ (Riedel de Häen). The blank-sample solution was prepared from 0.1 M HNO_3 (65% p.a. Merck 1.00456) and (KCl Merck 4935) of 0.2%.

Using ammonia buffer of pH = 9.25 (NH_4Cl; p.a. Merck 1.01145 + 25% ammonia) were prepared: chromate solutions (co-precipitation reagent 2; CR2, Fig. 1) from K_2CrO_4 (The British Drug Houses 0339280), sulfate solutions from $Na_2SO_4.10H_2O$ (p.a. Merck 6648), selenate solutions from Na_2SeO_4 (The British Drug Houses) and phosphate solutions from $Na_2HPO_4.12H_2O$ (Merck 6579). All solutions were diluted by Millipore water.

Digestion of samples

In order to concentrate all inorganic species from samples of pork liver, bovine liver and bovine bone a high-temperature-incineration procedure was applied. Initially, the samples were treated at 150 °C for 96 h, which expelled the water content before initiating the incineration. Subsequently, the bone samples were transferred to ceramic crucibles that were cleansed in ultrapure concentrated nitric acid. The bones were then incinerated at 1200 °C for 4 h. The liver samples were treated similarly with incineration at 400 °C during 3 h. Finally, the samples were ground in a mortar to a grain size of 0.2 mm. Samples of placebo, calcium and feeding stuff were ground directly without heat treatment. Samples of human hair were digested in a microwave oven by nitric acid, hydrogen peroxide and perchloric acid.[10,11]

The samples of bone, liver, hair, tablets, foodstuff and blanks were digested in a carefully cleansed quartz tube heated by a microwave oven (Maxidigest MX350). The samples were heated by a five-step procedure that included the addition of nitric acid and hydrogen peroxide: step (1) addition of 15 mL conc. HNO_3 and heating at 100 W power for 5 min, step (2) heating at 150 W power for 2 min, step (3) addition of 5 mL H_2O_2 (30%) and heating at 100 W power for 2 min, step (4) addition of 5 mL H_2O_2 (30%) and heating at 100 W power for 5 min., step (5) addition of 5 mL H_2O_2 (30%) and heating at 105 W power for 2 min. In order to be completely dissolved, the bone samples needed to be treated thrice by these five steps (48 min), while the other samples received double treatment. Undissolved solid remains were filtered off in the foodstuff and placebo samples. All samples and blanks were stored in polyethylene bottles.

Results and discussion

Under the optimised conditions, an enrichment factor (EF) of 24 and a concentration efficiency of 20 min^{-1} were achieved with the purpose of routine operation. By using longer loop lengths and stronger concentration of HCl and a longer time of pre-concentration, EF values close to 40 could be obtained (Fig. 2). Thus, the optimum conditions were applied, as to compromise between a high EF value and a high degree of repeatability, low uncertainties and a high sampling frequency. Under normal working conditions, the limit of detection (LOD, 3σ) was determined as 0.8 μg L^{-1} at a sampling frequency of 50 h^{-1}.

In order to test the system performance towards different anions and cations of the pre-concentration agent and towards the material of the KR, a number of experiments were conducted, as represented in Table 2. Significant variations were obtained from among the selected species and materials, albeit EF values between 1 and 2 were considered as being

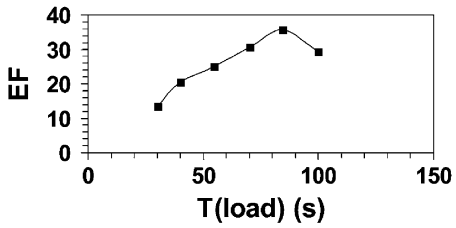

Fig. 2 The performance of the protocol with respect to enrichment factor that is depicted as a function of time of pre-concentration (*T*(load)).

Table 1 Optimum conditions of the FIA-pre-concentration protocol used for the analysis of barium

[HCl]/M	$[Pb^{2+}]$/M	$[CrO_4^{2-}]$/M	pH (CrO_4^{2-})	*T*(load)/s	*T*(inject)/s
2	0.002	0.100	9.25	60	10
Flow rate *Q*(HCl)/ mL min^{-1}	Flow rate *Q*(Ba^{2+})/ mL min^{-1}	Flow rate *Q*(Pb^{2+})/ mL min^{-1}	Flow rate *Q*(CrO_4^{2-})/ mL min^{-1}	KR	Length of KR/m
5	5	1	2	Nylon	0.100

Table 2 Investigation of cations, of anions and of KR-material influence on the performance of the protocol with respect to EF value. In the experiments with cation variation chromate was applied as the anion, while lead was used as the cation in experiments with substitution of the anion. The concentration of anions were 0.1 M while the concentration of cations were 0.002 M

Ion	EF (Nylon)	EF (Microline)	EF (PTFE)
Pb^{2+}	18.6	5.5	3.6
Cd^{2+}	1.5	1.5	1.7
Ag^{+}	1.3	1.3	2.1
Zn^{2+}	1.5	1.5	2.0
CrO_4^{2-}	15.3	4.6	2.9
SO_4^{2-}	2.0	1.6	1.6
SeO_4^{2-}	2.4	2.9	2.2
HPO_4^{2-}	6.9	2.7	1.8

insignificant. Thus, the results of Table 2 show that the higher EF values were reached by using nylon tubing for the KR and by applying lead chromate as co-precipitating agent. Significant EF values were obtained by using any of the three materials for the construction of the KR, which indicate that the nature of the co-precipitating agent is important for successful pre-concentration. It may also be deduced from Table 2 that hydrogen phosphate exhibits considerable pre-concentration efficacy, in comparison to the efficacy of the other anions. This may cause interference problems in the measurement of barium in samples with high phosphate concentrations. In addition to the measurements in Table 2, it was noted that no co-precipitation was obtained by using other group II elements, which demonstrate a high degree of selectivity of the barium determination.

In a series of experiments with a constant concentration of lead, $[Pb^{2+}] = 0.001$ M, the enrichment factor was investigated as a function of chromate concentration, as depicted in Fig. 3. A maximum EF value was found to exist at $[CrO_4^{2-}] = 0.1$ M and approached the value of unity only at very low chromate concentrations (Fig. 3). In a similar series of experiments with fixed chromate concentration and varying the concentration of lead, a maximum EF value was determined as $[Pb^{2+}] = 0.001$ M (Fig. 4). These findings show that the co-precipitation proceeds under non-stoichiometric conditions of lead and chromate, which may originate from differences in flow conditions of the FIA manifold, as compared with the physical flow pattern in knotted reactors.[12]

Although some of the species in Table 2 seemed to be slightly co-precipitated by the procedure, the change of EF value with concentration did not affect the pre-concentration efficacy except at high concentrations, *e.g.*, above 100 mg L^{-1} for zinc ions (Table 3). Thus, the measured EF values greater than one (Table 2), may be explained as a background level of pre-concentration, which was independent of the nature of the KR. However, the EF values of Cd^{2+}, Ag^{+} and Zn^{2+} were slightly improved by using PTFE reactors, which differed from the general trend of Table 2. By analysing samples of $[Ba^{2+}] = 0.1$ mg L^{-1}, the influence of interferences on the magnitude of the EF value were studied for a number of species, as shown in Table 3. The method tolerated relatively high concentrations

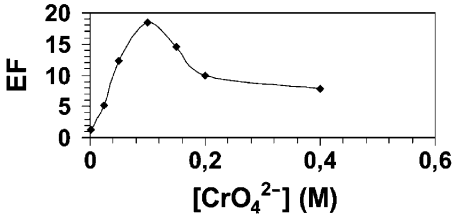

Fig. 3 The enrichment factor depicted as a function of lead concentration at $[CrO_4^{2-}] = 0.1$ M using optimised conditions (see Experimental). The load time was 60 s.

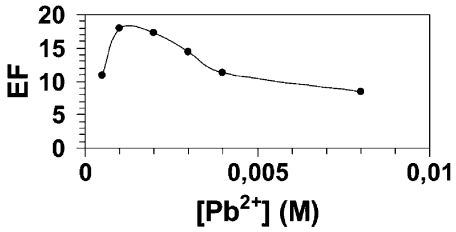

Fig. 4 The enrichment factor investigated as a function of chromate concentration at $[Pb^{2+}] = 0.001$ M using optimised conditions (see Experimental). The load time was 60 s.

Table 3 Investigation of interferences on the magnitude of EF by analysing a sample of Ba^{2+} at a concentration of 0.100 mg L^{-1}

Interference species	Level of significant reduction of EF/mg L^{-1}
Ca^{2+}	115
Mg^{2+}	200
NaCl	300
Fe^{2+}, Fe^{3+}	1
Zn^{2+}	100
Cu^{2+}	90

of sodium, magnesium and chloride while iron species, in both common oxidation states, posed a high influence. Thus, iron species constitute the prime interference and the limit where the iron content began to significantly reduce the magnitude of the EF was approx. 1 mg L^{-1} (Table 3). Species of calcium, copper and zinc reduced the EF value significantly at concentration levels of approx. 100 mg L^{-1}. These results show that the method is well suited to pre-concentration of barium in saline waters and, tentatively, may be applied to matrices that are more complex. In biological matrices, the level of iron is below 1 mg L^{-1}, which justifies application of the method to direct analysis of barium without extensive sample pre-treatments. Thus, the method was applied to analysis of barium and in saline water, in natural water and in biological samples, as shown in Table 4. The content of barium in human hair was found to be close to the limit of detection of the protocol, which was less than found in other hair samples, as reviewed by Iyengar and Iyengar.[13] This discrepancy may readily be explained by normal biological variations, however, the content of barium in the bone samples does not correspond to the level of barium found in, *e.g.*, human bones, as determined by Yoshinaga *et al.*[14] A factor of 200 more barium was found in bovine bone, as compared with the barium content of human bones. The deviation, of course, might be a result of the difference in biological species but it could also be related to differences in the procedure of digestion. In the present work, the samples were subjected to an incineration protocol that led to a complete removal of all organic material, which indicate that significant amounts of barium could be extracted by high-temperature treatments. Tentatively, unless carefully digested at high temperature, there is a risk of loosing some of the barium to the solid remains separated from the sample by filtering. In bone, the barium content corresponded to the content found in calcium tablets, which was also expected owing to the companionship of calcium and barium. Much less barium was found in therapeutical placebo medicine where the barium content was reduced to 0.3 μg g^{-1} dry weight, which shows that the tablets were prepared by high-purity calcium. The high selectivity with respect to barium analysis in matrices of other group II metals is an attractive property of the method, as compared with methods based on *e.g.* ion-exchange.[15,16]

Although the barium content of local drinking water was relatively high reaching values of 70 μg L^{-1}, it did not exceed the limit of 100 μg L^{-1}. The bottled water samples contained

Table 4 Analysis of barium in various samples by the method, as developed

Sample	$[Ba^{2+}]$/μg g^{-1} (dry weight) or μg L^{-1} (water samples)	Determination by ICP-MS $[Ba^{2+}]$/μg g^{-1} (dry weight) or μg L^{-1} (water samples)
Bovine bone	260 ± 10	—
Bovine liver	0.44 ± 0.05	0.9 ± 0.4
Pork liver	0.34 ± 0.05	—
Placebo tablet	0.30 ± 0.05	—
Calcium tablet	260 ± 10	—
Foodstuff	1.7 ± 0.1	—
Seawater (Øresund, Denmark)	40 ± 2	—
Drinking water (local)	70 ± 2	62 ± 2
Bottled water 1 (commercial product)	5 ± 1	3 ± 6
Bottled water 2 (commercial product)	21 ± 1	27 ± 9
Bottled water 3 (commercial product)	13 ± 1	12 ± 7
Bottled water 4 (commercial product)	11 ± 2	14 ± 7
Hair, male, 80 years of age	Not traceable	0.7 ± 0.5
Hair, male, 42 years of age	Not traceable	0.4 ± 0.2
Hair, male, 23 years of age	Not traceable	0.5 ± 0.2
Hair, male, 22 years of age	0.2 ± 0.1	0.4 ± 1
NIST SRM 1640, $[Ba^{2+}]$ = 148 ± 2	150 ± 10	155 ± 5

much less barium, as compared with the content of drinking water.[15] Further, the barium content of the bottled water samples was different because they originate from different sources. The samples of foodstuff and liver contained low amounts of barium and no significant differences were observed between the pork and bovine samples. The barium content of the standard reference material (NIST SRM 1640) was determined with satisfactory precision albeit the greater standard deviation, as compared to the certified value. The concentration of barium in seawater was determined as 40 μg L^{-1} (Table 4), which is a value that was less than found in drinking water. Since the study of interferences in Table 3 showed that the protocol tolerated high levels of salt, as in seawater, it thus supports the reliability of the result. Some of the samples were also analysed by ICP-MS (PerkinElmer, Elan 5000) and the results are given in Table 4 (second column). For the sake of comparison, the samples, except the NIST SRM 1640 and drinking water, were analysed directly, without pre-concentration, by the protocol Totalquant II (PerkinElmer), which allows determination with preparation of only a single standard solution. By using this protocol, the results were subjected to a relatively high level of uncertainty (Table 4) but none of the results violated the credibility of the present method. The ICP-MS results showed that the samples of human hair did contain traces of barium, which was not detected by pre-concentration. The NIST SRM 1640 and the drinking water was analysed using two standards by ICP-MS/ Quantitative Analysis (PerkinElmer) and thus determined with good precision in agreement with the results of the pre-concentration method.

The mechanism of pre-concentration by co-precipitation is related to both chemical and physical properties of the system. Previously, methods of filterless pre-concentration by co-precipitation were based on inclusion of the analyte species into a gelatinous precipitate of a suitable hydroxide such as $Al(OH)_3$[6] or $La(OH)_3$.[7] In the present work, pre-concentration by $La(OH)_3$, $Al(OH)_3$ and $Mg(OH)_3$ was also tested but they all proved ineffective. Since lead chromate was found to be the sole effective co-precipitating agent, the mechanism of pre-concentration must differ from the principle of inclusion. Lead chromate is a well-defined-crystalline substance and barium is well known to be co-precipitated in batch experiments, where barium is substituted for lead in the crystal lattice, owing to the similarity of ionic radii. Thus, by occupying lattice sites of lead, the barium may be co-precipitated, where adequate adhesion of the lead chromate to the walls of the reactor is compulsory. The experiments of Table 2 clearly demonstrated that the choice of material of the knotted reactor was very important with respect to efficacy of pre-concentration. Thus, nylon was found to possess adequate hydrophilic properties, as to interact strongly with the precipitate of barium lead chromate. The chemical observations correspond to the predictions of Paneth–Fajans–Hahns rule[6] and Paulings observation.[6] The rule of Paneth–Fajans–Hahn states that pre-concentration is promoted by a large surface area of the crystallites and by a low solubility of the salt formed by the analyte. Thus, barium must form an insoluble compound with the anion of the co-precipitant, as with chromate. Paulings observation is related to the similarity in charge density of the ions of the lattice. The ionic radius of barium is 1.35 Å and that of lead ions is 1.20 Å, which are relatively comparable, as to yield similar charge densities. Although the ionic radius of *e.g.* strontium is closer to the ionic radius of lead, it does not form an insoluble chromate, which thus violates the Paneth–Fajans–Hahns rule. Similarly, despite the fact that silver forms an insoluble salt with chromate ions, the charge density is very different from that of lead; this violates the Pauling observation and was also confirmed experimentally.

Conclusion

It was demonstrated that barium could be pre-concentrated by co-precipitation of lead chromate prior to analysis by FIA-FAES. The method is based on filterless pre-concentration in a knotted reactor of nylon material. It is a novel example of filterless pre-concentration by co-precipitation where a crystalline material was formed during the analysis procedure. Thus, it may be suggested that the protocol could be optimised, as to also encompass other crystalline systems. The method was highly selective and allowed direct analysis of barium in saline water and other matrices with iron species being the prime source of interferences. Plausible results were obtained by analysing real samples of drinking water, seawater and a standard reference material where barium was found within the μg L^{-1} range level of concentrations. Analysis of complicated organic matrices such as bone required careful incineration that promotes full extraction of the analyte. The FIA manifold used in the protocol may also be applied to other detection systems such as inductively coupled mass spectrometry by which much lower detection limits may be achieved.

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