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LECTURE

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Investigation of the IC-ICP-MS determination of iodine species with reference to sample digestion procedures

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Abstract The determination of iodine in aqueous solutions suffers from several serious problems, caused by the formation of iodine species, derived from the oxidative pretreatment of biological materials. For the determination of these iodine species an ion chromatograph was coupled with an ICP-mass spectrometer. Because of the possible interconversion of the iodine species depending on the pH-value, different eluent-column combinations were used for acidic or alkaline sample solutions, respectively. Iodide, iodate, and several not identified, presumably organo-iodine species could be separated and detected. Unfortunately, the iodine (I_2) itself could not be determined with the method proposed. The reaction products of pretreatment are influenced strongly by the matrix. Mixtures of different iodine containing components are received, dependent on the matrix composition and particularly on the pH-value.

Introduction

Iodine is an essential trace element [1, 2]. Methods for the determination of iodine traces are the catalytic method [3–5], neutron activation analysis [6–8], electrochemical methods [9, 10], ICP-OES [11, 12], MIP-OES [13], ICP-MS [14–17], ion chromatography [18, 19], and HPLC [20], as well as ICP-MS coupled with chromatographic separation [21, 22].

However, iodine determination is reported to suffer from special difficulties [15, 17]. The composition of the reaction products, yielding from the sample pretreatment procedure, strongly influences the analytical result. Elementary iodine (I_2) can easily be formed in solution, e.g. according to the following equation:

$$IO_3^- + 5\ I^- + 6\ H^+ \rightleftarrows 3\ I_2 + 3\ H_2O \quad (1)$$

This can lead to analyte losses, to carry-over, and memory effects, as well as to significant sensitivity alterations in pneumatic nebulization ICP-MS.

The coupling of ion chromatography with ICP-MS was applied to the characterization of these reaction products, in order to improve the procedure of iodine determination.

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Experimental

Microwave assisted digestion of standard reference materials

A pressurized microwave assisted digestion procedure was carried out by the MDA-II (Berghof-Maassen Laborprodukte) in PTFE-digestion vessels (capacity: 150 mL). Two biological reference materials were used: BCR 151 “Spiked Skim Milk Powder”, certified iodine concentration 5.35 ± 0.14 mg/kg, and BCR 279 “Sea Lettuce (Ulva Lactuca)”, indicative iodine concentration 149–158 mg/kg.

About 1.5 g of the biological material were mixed cautiously with 10 mL HNO_3 (65%, suprapure, Merck) and 5 mL H_2O_2 (30%, suprapure, Merck). Microwave power ($P \leq 400$ W) was applied for 30 min, achieving about 220°C under elevated pressure ($p \leqq 8$ MPa). The resulting solutions were transferred into volumetric flasks (50 mL) and diluted to volume with water.

IC-ICP-MS: Species analysis of iodine in aqueous sample solutions

For the speciation of iodine an ion chromatograph DX-100 (DIONEX) was coupled with an ICP-MS device ELAN 5000 (Perkin-Elmer SCIEX). The flow rate of the eluent was chosen to be 1.5 mL/min using the HPLC-pump of the DX-100. The sample volume was 0.025 mL. The chromatograms were recorded in the graphic-mode by 1200 readings on mass 127 with dwell-time of 1500 ms. The nebulizer gas flow rate has to be adjusted according to the eluent used.

Iodine is subjected to pH-depending redox equilibria in aqueous solution which are adjusted considerably fast. In order to stabilize the original species composition during the chromatographic process an eluent has to be chosen, which is similar to the sample solution, at least in pH.

For the acidic samples the following eluent composition was applied: 20 mmol/L HNO_3 and 50 mmol/L $NaNO_3$ (Eluent A: pH ~ 1.7), using the column AS7 (DIONEX) . The samples with ammonia added, which was recommended prior to analysis in order to minimize the mentioned difficulties [15], were preferably analyzed with an eluent composition of 5 mmol/L Na_2CO_3, 40 mmol/L NaOH, and 8% methanol (Eluent B: pH ~ 12.5), using the column AS4A-SC (DIONEX).

With both chromatographic systems the species iodide and iodate could be detected baseline separated. However, the detection of iodine (I_2) itself was not accomplished.

Results and discussion

Investigations using pneumatic nebulization ICP-MS

Preliminary investigations using pneumatic nebulization ICP-MS resulted in identical sensitivities for iodide and iodate in identical matrices. In 3% ammonia solution the sensitivity was found to be 830 cps/μgL^{-1}. In urine a decrease in intensity to 37% was obtained, compared to the ammonia solution. After adding nitric acid up to a concentration of 1% the intensities were found to be enhanced to 120% compared with the appropriate non-acidified matrices.

Speciation of iodine by IC-ICP-MS using Eluent A (pH ~ 1.7)

In Eluent A the iodate signal appears at t_r ~ 100 s, the iodide signal at t_r ~ 1000 s.

In contrast to the calibration in Eluent B, the iodide signal was found strongly diminished compared to the iodate signal. The explanation for this difference in sensitivities is seen in the synproportionation reaction according Eq. (1). If this reaction occurs, the decrease of the iodide signal should be 5 times the decrease of the iodate signal. Following that assumption an overall sensitivity could be calculated: e_A ~ 1375 cnt/μgL^{-1}.

The chromatograms of the acidic solutions of the BCR 151 and the BCR 279 show only iodate signals in both cases. The concentrations obtained are summarized in Table 1.

In the case of BCR 151 the recovery is about 100%, apparently the oxidizing acidic solution was able to convert the entire iodine into the iodate. In the case of BCR 279 the recovery was found worse, supposing that molecular iodine was formed, which could not be separated and detected by the chromatographic system.

During the oxidizing acidic digestion procedure iodate and presumable I_2 are formed, whereas their amounts, and therefore the analytical results, are dependent on the matrix composition.

Table 1 Results of IC-ICP-MS analysis of standard reference materials

Sample	pH	Iodine found [mg/kg]	Recovery [%]
BCR 151[a]	1.7	5.3	100
BCR 151	12.5	4.0	75
BCR 279[b]	1.7	60	40
BCR 279	12.5	70	45

[a] BCR 151: Spiked Skim Milk Powder, C_I (certified value) = 5.35 ± 0.14 mg/kg
[b] BCR 279: Sea Lettuce (Ulva Lactuca), C_I (indicative value) = 154 mg/kg

Speciation of iodine by IC-ICP-MS using Eluent B (pH ~ 12.5)

Using Eluent B iodate (at t_r ~ 60 s) and iodide (at t_r ~ 320 s) gave similar signals with equal sensitivity: e_B = 2400 cnt/μgL^{-1}.

When the digestion procedure was applied to pure NaI-standard solution, in the alkalinized sample only iodate could be detected by IC-ICP-MS. In the solution derived from digestion of BCR 151 (Milk Powder) high amounts of iodate besides very small ones of iodide were observed in alkaline medium. Amazingly, after the sample preparation of the BCR 279 (Sea Lettuce) iodide was detected, whereas an iodate signal was not recognizable. The concentrations, given as iodine, are summarized in Table 1.

The comparison of the results in acidic and alkaline media shows, that the addition of ammonia solution may change the composition of iodine species. However, it can not entirely solve the problems, once volatile I_2 occurred in the sample solution, which is responsible for unsatisfactory recoveries.

Speciation of iodine in urine samples by IC-ICP-MS

Samples of so-called “untreated“ urine being urine without any reagents added, urine to which 500 µL of conc. H_2O_2 are added to 50 mL of sample, and urine to which 500 µL of conc. H_2O_2 as well as 500 µL of conc. HNO_3 to 50 mL of sample are added were analyzed.

When untreated urine was analyzed immediately, the chromatogram using Eluent B shows only almost iodide (Fig. 1a). However, when this urine was stored overnight at room temperature, the iodide signal decreased and the iodate signal increased (Fig. 1b). Obviously, iodide was oxidized to iodate, probably by air. The sum of the concentrations of iodate and iodide was found to be about 90 µg/L in both cases.

If the urine was preserved and acidified, the oxidation process was obviously accelerated, indicating a higher concentration of iodate formed overnight. Between the iodate and iodide signals an “increased background“ appeared (Fig. 2a). The overall iodine concentration was found to be 67 µg/L.

By addition of hydrogen peroxide only (Fig. 2b) the iodide signal disappeared almost completely. The iodate signal increased. Additionally a number of peaks appeared, probably caused by iodine-containing oxidation products of urinary organic compounds. The overall iodine concentration was calculated to be about 65 µg/L.

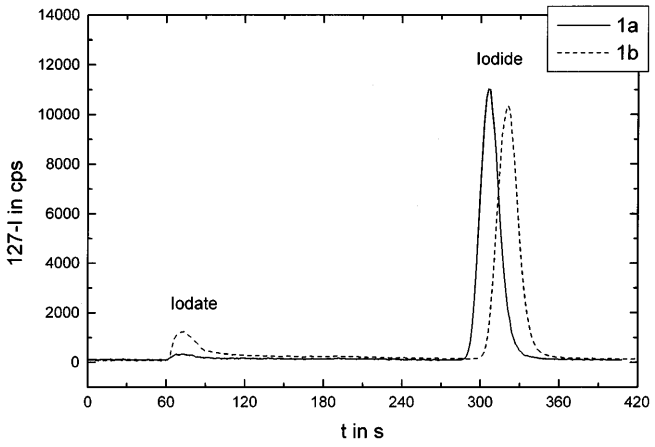

Fig. 1 IC-ICP-MS: Eluent B, pH ~ 12.5, Column AS4A-SC; *1a* Urine, untreated, analyzed immediately; *1b* Urine, untreated, stored at room temperature for 24 h

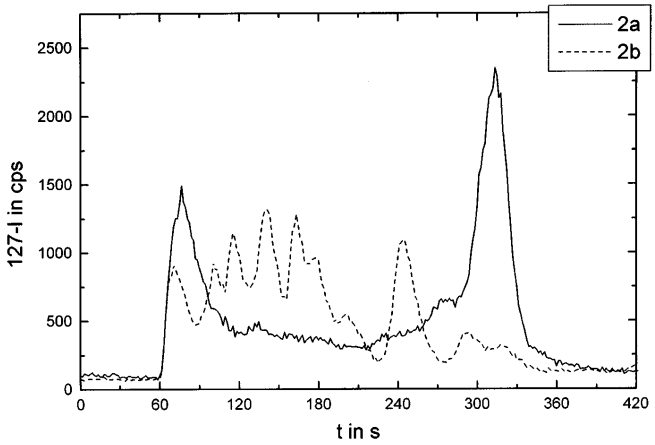

Fig. 2 IC-ICP-MS: Eluent B, pH ~ 12.5, Column AS4A-SC; *2a* Urine, preserved with hydrogen peroxide, acidified with nitric acid; *2b* Urine, preserved with hydrogen peroxide

Comparing the overall concentrations of the iodine species in untreated and preserved/acidified urines, respectively, the reduction in the latter cases may be pointed out to the formation of iodine-containing compounds, which could not be detected in the chromatogram.

If untreated urine was analyzed immediately in Eluent A, a remarkable part of the iodide disappeared. On the other hand, the rising signal for iodate suggests, that the iodide has been instantly oxidized to iodate just before the separation takes place. This is attributed to a fast attainment of the equilibrium.

In preserved and acidified urine, respectively, iodate was found as the major component, together with other iodine-containing species. Iodide could not be observed.

Multielemental analysis including iodine in urine

For the simultaneous determination of iodine and trace metals by pneumatic nebulization ICP-MS three different acidified and preserved urine samples were analyzed using standard addition calibration (SAC). Because the analysis of the preserved urine showed that iodine was present mainly as iodate, the samples were spiked with iodate together with 15 trace metals. Rhenium was used as an internal standard.

According to the chromatographic results the iodine in untreated urine was present as iodide solely. Therefore, the determination using standard additions (SA) with iodide-spikes could be established, producing reference concentration values for the validation. The recoveries were calculated from the concentrations obtained after applying the SAC multielemental procedure and related to the reference concentrations using the SA procedure. The recoveries were found to be in the range from 95% to 110%, being entirely sufficient for a screening analysis in urine.

Conclusion

The results using IC-ICP-MS show that different iodine species were obtained depending on the sample composition and the applied sample preparation procedure. Iodide, iodate, and in some cases not identified organic iodine-containing compounds were qualitatively found in the sample solutions. The quantification of these species is difficult, particularly in acidic solution.

Unfortunately, the detection of iodine (I_2) itself was not successful by the analytical procedures used. However, it was presumed from the experimental results, particularly from the conversion of iodide into iodate in acid matrix, that iodine (I_2) can be formed in the resulting solutions after oxidizing digestion.

By addition of ammonia solution prior to analysis iodate and iodine can be converted into iodide. However, elementary iodine (I_2) may still remain in the system and interferes the analysis. On the other hand, the addition of ammonia is unfavorable with regard to analysis of trace metals, in that way the capability of ICP-MS is limited for multielemental analysis.

In untreated and in acidified/preserved urine samples the simultaneous multielemental determination including iodine is possible by pneumatic nebulization ICP-MS using the method of standard addition calibration.

Further work will be devoted to substances, which could stabilize the iodine in the sample solutions, resulting in matrix modifiers for multielemental ICP-MS analysis of aqueous solutions.

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