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Analysis of iodine species in aqueous solutions

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Abstract Iodine is a biologically important trace element. Its behaviour in the environment and in human metabolism is determined by the type of iodine species which takes part in chemical reactions. Knowledge of their concentrations is necessary to understand and describe the iodine reaction paths. A separation procedure is proposed for quick determination of common forms of iodine—iodide, iodate ions, molecular iodine and organoiodine (in the form of CH_3I). The procedure consists of sequential sorption by passing the sample solution first through a solid-phase extraction cartridge to separate I_2 and CH_3I from IO_3^- and I^- then through an anion-exchange resin in a cartridge to retain the latter two species. Each loaded cartridge is eluted to separate the sorbed pair of species. Concentration determination of the resulting four solutions can be performed by standard methods, e.g. by spectrophotometry, tracer counting or with ion-selective electrodes.

Keywords Iodine species · Analysis · Separation · Solid-phase extraction · Ion exchange

Introduction

Iodine is one of the most important trace elements in food. Iodine-containing pharmaceutical products are often used in medical diagnostics and therapy. The stable isotope ^{127}I occurs naturally and the long-lived radionuclide ^{129}I (half-life 10^7 years) is formed in natural nuclear reactions, but it is also a main fission product of uranium and plutonium in nuclear reactor power plants [1]. The determination of the isotope ratio $^{129}\text{I}/^{127}\text{I}$ [2] gives important information about the source of the iodine, its identification and distribution in the environment.

Iodine-containing samples were usually treated prior to analysis by converting the iodine species first to molecular iodine, evaporation and trapping in solution, followed by reduction to iodide. The concentration determination was then performed by absorption photometry or by using iodide ion-sensitive electrodes. In some cases, direct quantitative iodine determination by activation analysis was possible. Ion-chromatography and expensive or complicated multistage separation procedures, which include several liquid/liquid extraction or precipitation steps, were also used [2].

The presented analytical method for complex mixtures of iodine species consists of a combination of successive species extraction or sorption on selected solid phases, i.e., modified silica, anion-exchange resins and activated charcoal (either in column or cartridge form). The concentrations of the eluents are then determined by well-known standard methods. The method is specifically designed to determine iodide, iodate, molecular iodine and organoiodine (especially CH_3I) aqueous concentrations and, if present, the CH_3I and I_2 concentrations in the gas space above the solution. It can be applied to iodine concentrations, which range from 10^{-6} (iodide concentrations from 10^{-8}) to $10^{-2} \text{ mol L}^{-1}$.

The method can be used to routinely analyse samples taken from, for example, industrial processes or natural water reservoirs. It offers a rapid and simple analysis using standard cartridges. The solid phase filters may also be part of an automated at-line monitoring of iodine species in reactions, for example, in experiments to investigate the radiolysis and the hydrolysis of organoiodine.

Diversity and stability of iodine species

In aqueous solutions or in a gas atmosphere, many different iodine species can exist, since iodine can form compounds in all oxidation states from -1 to $+7$.

The hydrolysis of molecular iodine to form hypoiodous acid (HOI), following rapid equilibrium involving intermediate species is an important reaction in the ab-

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sence of radiation. The overall stoichiometry is shown in Eq. (1). HOI disproportionates according to the stoichiometric reaction depicted by Eq. (2) to form iodate. These two reactions combine to give the summary reaction depicted by Eq. (3). Molecular iodine is only significant under acidic and oxidizing conditions, since the equilibria are shifted to the left. Conversely, iodide and iodate can only co-exist in neutral and basic solutions. HOI dissociates significantly at high pH (>10) to form the hypiodite ion, OI^- (Eq. 4).

The hydrolysis reaction is temperature-dependent; the I_2 -fraction decreases by about 100× when the temperature is increased from 25 °C to 100 °C over a range from about pH 5 to 10. Molecular iodine is also in rapid equilibrium with iodide to form the triiodide complex I_3^- (Eq. 5).

Numerous redox reactions can also take place, for example, with the products of water radiolysis, i.e., with the radicals $\cdot\text{OH}$, $\cdot\text{H}$ and the solvated electron, e_{aq}^- , as well as other products, such as H_2O_2 , HO_2 and O_2^- (the last is formed by reducing dissolved O_2 with e_{aq}^-). Iodide is oxidized by $\cdot\text{OH}$ radicals, via several steps, to form volatile molecular iodine. However, the yield is dependent on the balance between competing oxidation and reduction reactions. These reactions are controlled by the experimental conditions, such as pH, temperature, total iodine species concentrations, dissolved oxygen, impurities and radiation dose. For example, although H_2O_2 is relatively slowly produced, HO_2 , which is formed by H_2O_2 oxidation, rapidly reduces I_2 or its hydrolysis product HOI in alkaline solutions, especially in the presence of borate [3].

Iodine species analysis is routinely restricted to some of the species with the most stable valance states, that is, iodide (−1) and iodate (+5). Molecular iodine and organoiodine compounds are also determined. However, if the reaction conditions at the time of sampling are not considered, the long-term storage of samples could lead to a different composition of iodine species. The results of their determinations would then be invalid.

Due to the recognized complexity of iodine chemistry, computer codes were developed to model the many reactions between iodine species. An example of one approach in order to predict their integral effect is to reduce the number and simplify the reactions to a few but important species [4]. The stability of each iodine species can then be estimated.

Separation of aqueous iodine species

To find and test the conditions for optimum separation of the iodine species, the radioisotope ^{131}I tracer was used.

The activity measurements allow a rapid, direct and sensitive determination of the iodine species distribution after their separation into fractions. The technique generally allows a species concentration range from 10^{-8} to $10^{-2} \text{ mol L}^{-1}$ using the tracer activity levels of our investigations.

Solid-phase filter cartridges were first tested only with aqueous mixtures of iodide and iodate ions before separation of the neutral compounds (molecular iodine and methyl iodide) was investigated.

Anion-exchange resin cartridges with quaternary ammonium functional groups were chosen for the iodide–iodate ion separation. Both these anions, in a solution of pH range from 5 to 10, were sorbed on the top layers of the exchange resin in the filter cartridges. Experimental results have shown that iodate and iodide ions can be separately eluted by exploiting their different sorption affinities. Iodate is first eluted by passing 2 mL of $5 \times 10^{-3} \text{ mol L}^{-1}$ NaOH through the cartridge (type: QMA / Waters Corporation, USA), iodide ions are then desorbed with the first mL of 0.2 mol L^{-1} NaOH.

By using solid-phase extraction cartridges, separation of I_2 and CH_3I was achieved by exploiting their differing extraction (sorption) affinities. Selective removal from the solid phase was attained with the following procedure. Starting from a sample solution in the pH range 5–10, I_2 and CH_3I

Fig. 1 Procedure for selective one-species separation of samples containing two or more iodine species in aqueous solution: iodide, iodate ions, molecular iodine, organoiodine (RI, e.g. methyl iodide)

Fig. 2 Ion chromatographic analysis of iodate and iodide ions in aqueous solutions of boric acid/sodium borate (IO_3^- : 18 ppb/ I^- : 26 ppb at pH 5, 44 ppb at pH 8)

were “fixed” on the cartridge (type: LiChrolut RP18; Merck, Germany). By passage of a solution of either 2 mL 0.1 mol L^{-1} sodium thiosulfate or sulfite in 0.1 mol L^{-1} sulfuric acid solution, I_2 was then reduced to iodide. The methyl iodide was then desorbed by passing 2 mL methanol through the cartridge.

Finally, a separation procedure for all four iodine species by combining the two methods was successfully obtained (see Fig. 1), under the mentioned conditions in order to retain their stability in the sample solutions.

After elution, the collected fractions can be analysed for iodate, by adding an excess of iodide in buffer solution ($\text{pH} \leq 4$) to form triiodide ions (I_3^-) due to iodide oxidation by the iodate [5]. Iodide, either directly or as reduction product from other iodine species can be measured with an ion-selective electrode [6]. In special cases, activation analysis with neutrons from research reactors can also be used. To monitor contamination in the environment, due to the long-lived iodine fission product ^{129}I , distribution mass separation analysis can be performed. The highest sensitivity is achieved by the use of accelerator mass spectrometry (AMS) [7]. When iodine radionuclides are present or the expected sample concentration is sufficient (concentration levels of ppb or more), the iodine content can be directly determined in solution or on the sorbent by gamma or X-ray measurements respectively.

The proposed solid-phase extraction method can be modified to analyse iodine species also in the gas phase, by dissolving or by sorbing them in water or on to a solid phase. Their subsequent separation is explained below.

Results of additional experiments show that ion-chromatographic determinations of low (ppb) iodide and iodate concentrations in aqueous solutions of boric acid (pH 5)/sodium borate (pH 8) can be performed. The method is also extendable to iodine species determinations in the presence of other anions. An example (Fig. 2) shows that ppb levels of iodide and iodate can be determined in the presence of about 2 ppm concentrations of chloride and nitrate.

In dilute sulfuric acid (pH 2) and sodium hydroxide (pH 12) solutions, iodide ions retain their position at the end of the elution volume. The retention time of iodate at both pH values is about 2.5 min, but in acid solutions iodide cannot co-exist with iodate, due to iodide oxidation by the latter. The stability of iodine species is discussed above.

If molecular iodine is present, then the sample solution must first be passed through a solid-phase extraction pre-column to retain it, reduced with thiosulfate and removed (see above). In a second ion-chromatographic run, the newly-formed iodide was separated from the thiosulfate [8]. Its concentration was then either determined by conductivity (Fig. 2) or by activity measurements if the species were previously tagged with ^{131}I radionuclide.

Quick test and automated iodine species analysis

The cartridge technique in combination with the proposed species separation procedure can be easily adapted to routine environmental control. This fast and efficient analysis can be used for “quick tests”. In addition, the technique provides a good basis to develop an automated analysis for multi-iodine species.

For example, irradiation experiments on the behaviour of methyl iodide in solution, tagged with ^{131}I , are being performed at the Paul Scherrer Institute. The described method allows an at-line analysis of the process. Fig. 3 shows a schematic of the facility, which allowed monitoring of methyl iodide, molecular iodine (both in the aqueous and gas reaction spaces) as well as iodide and iodate ions in the aqueous sample solution. Automated sampling after different reaction or irradiation periods has allowed the monitoring of a series of experiments, which used different initial concentrations (from 10^{-6} to $10^{-2} \text{ mol L}^{-1}$) of methyl iodide in the presence of boric acid (0.25 mol L^{-1}).

Determination of molecular iodine and methyl iodide in the gas phase was effected by displacing them with ar-

Fig. 3 Schematic set-up of an at-line analysis of iodine radiolysis products of methyl iodide by selective iodine gas and aqueous species sampling followed by iodine concentration determination (V1/V2: valves to switch the sampling from gas, V1, (displaced by Ar) to solution, V2)

gon into specialised solid-phase materials in a cartridge or column for sorption. By placing the cartridges in series, I_2 is sorbed first on modified silica (DSM11; Sud-Chemie,

Germany) then CH_3I is sorbed in tetraethylenediamine-impregnated (TEDA) activated charcoal (Sutcliffe Speakmann Carbons, UK). If the iodine is sufficiently tagged with ^{131}I , then the activity in the cartridges can be directly measured.

The aqueous iodine species were separated into two fractions, neutral and ionic, in two steps (Fig. 3). If all four species were present, then single species fractions were prepared in subsequent steps for measurement (Fig. 1). Several sampling lines can be used to monitor multiple experiments simultaneously by using remote-controlled valves. Furthermore, the analytical technique can be applied to studies associated with nuclear safety, for example, monitoring iodine mitigation processes and fission product waste and storage problems.

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