Ion chromatographic analysis of aqueous iodine species by conductivity and radioactivity measurements

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Summary. A new device was developed for the identification of several iodine species in aqueous solution using ion chromatography. Iodide, iodate and molecular iodine can be determined. (The equipment allows both conductivity and radioactivity detections.) The method is applicable for the determination of radioactive iodine contaminations in the cooling water of nuclear power plants.

Introduction

Iodine is one of the most essential trace elements in food. The stable isotope ^{127}I occurs naturally and, together with the long-lived ^{129}I and the shorter-lived ^{131}I , is generated as one of the main fission products of uranium and plutonium during nuclear power plants (NPP) operation [1]. Its release into the reactor containment or, especially into the environment as a result of an accident can represent a significant safety issue. One of the problems associated with the iodine is to know its chemical forms and to understand the corresponding reactions in water, in the reactor containment, the environment and during its long-term waste disposal, in order to describe its behaviour. The knowledge of the iodine chemistry and the retention mechanisms of radioactive iodine isotopes is a main premise concerning the safety requirements of a nuclear reactor containment in the case of a severe accident.

For the high sensitive iodate and iodide analysis, and in particular for post (off-line) test analysis of silver iodide radiolysis reaction products and for specific iodine mitigation experiments, an ion chromatography (IC) method was developed and introduced into the analytical practice. These iodine specification analyses are essential for the investigation of the volatility behaviour and the release minimisation of radioactive iodine isotopes in NPP.

IC is a well-established technique for many applications [2], but iodine was analysed only as the sum by reduction of all species to iodide [3,4]. Only Bichsel *et al.* [5] reported on the determination of iodide and iodate by ion chro-

matography with postcolumn reaction and UV/visible detection. Iodide/iodate separations are up to now not considered in standard applications of companies like METROHM or WATERS. Additionally, complications arise from the presence of boric acid/borate buffers, which are essential for cooling water of NPP [6]. Thus, a method was developed which allows both the determination of many different anions and of iodine species (iodide, iodate and molecular iodine) simultaneously in one run by measurement of the total conductivity and detection of their radioactivity. For cooling water analysis, this equipment is required for impurity control.

Experimental and equipment

The setup of the system developed for simultaneous IC analysis of radioactive iodine species and other anions is shown in Fig. 1. Isocratic elution was carried out with a METROHM column (Metrosep A-Supp 5-250) using a carbonate-bicarbonate solution as eluent. Conductivity detection (Typ 732 IC detector) was performed with a suppression module (MSM IC Type 753), 0.05 M H_2SO_4 .

Fig. 1. IC equipment for simultaneous conductivity and radioactivity measurement.

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For the radioactivity measurement, a new CsI(Tl) scintillation detector (Carroll Ramsey, Berkeley, USA, System Model 105-S-2) was used, which gives an essential improvement of the signal/noise ratio at energies above 300 keV. Thus, solutions with an activity level in the range of kBq can be analysed. Standards were prepared in bi-distilled water and in boric acid/borate solutions at pH 5–11.

Results and discussion

The developed iodine analysis method can be applied to a wide spectrum of sample types. In Figs. 2a and b the ion chromatograms of iodide and iodate (1 ppm each, spiked with 200 kBq ^{131}I tracer solution) together with a selection of other anions, are shown using the conductivity and radioactivity detectors simultaneously for measurement. The ion mixture was dissolved in the eluent solution before injection. In the chromatogram measured by conductivity a sufficiently symmetric shape of the peaks and a clear separation of all anions could be obtained. The chromatogram obtained

Fig. 2. IC analysis of several anions in eluent solution, 1 ppm iodide and iodate, respectively, at pH 10.3, eluent: 3.2 mM Na_2CO_3 /1 mM NaHCO_3 ; flow: 0.7 mL/min, column: A Supp5-250 from METROHM (Switzerland), (a): conductivity detector with suppression; (b): radioactivity detector.

by radioactivity measurement shows also a clear separation of iodide and iodate. Since no interference with other anions is possible using radioactive tracers, the iodide/iodate ratio of this solution can be calculated very simple and with high accurateness.

In Figs. 3a and b, the chromatographic behaviour of a pure iodate/iodide mixture (1 ppm each) in the presence of boric acid/borate at different concentrations is shown. The measurements were performed only by use of the conductivity detector. Peaks of NO_3^- and SO_4^{2-} are also observed in this solution, but they are of minor importance because they do not influence the analysis of the iodine species. At relatively low concentration (0.005 M, Fig. 3a), the boric acid does not much affect the peak shape, but a slight change of the basic line is observed. The higher concentration (Fig. 3b, 0.03 M boric acid/borate) influence the peak form and, especially, the peak area, dramatically, so that an accurate determination of the iodide/iodate ratio becomes difficult. The situation is worse, if other anions are present in the solution under investigation, as can be seen in Fig. 4a. Here, a mixture of again 1 ppm iodide/iodate, respectively, and several other anions in the presence of 0.02 M boric acid/borate is measured with the conductivity detector. The determination of the iodide/iodate ratio is still possible due to the sufficient peak resolution, but, as can be seen in Fig. 4b

Fig. 3. IC analysis of a sample solution containing iodine and other anions in the presence of several boric acid/borate concentrations, 1 ppm iodide and iodate, respectively, measured with a conductivity detector, pH 10.3, eluent: 3.2 mM Na_2CO_3 /1 mM NaHCO_3 , column: A Supp5-250 (METROHM); (a): 0.005 M borate; (b): 0.03 M borate.

Fig. 4. IC analysis of several anions in 0.02 M borate solution, 1 ppm iodide and iodate, respectively, at pH 10.3, eluent: 3.2 mM Na_2CO_3 /1 mM NaHCO_3 ; flow: 0.7 mL/min, column: A Supp5-250 from METROHM (Switzerland), (a): conductivity detector with suppression; (b): radioactivity detector.

(identical solution as used for the experiment in Fig. 4a, but spiked with 200 kBq ^{131}I tracer solution), a much better calculation can be done by use of the radioactivity detector. Thus, in cases where iodine has to be analysed in solutions with high bulk content or buffer solutions, as it occurs regularly in the liquid waste of NPP, the radioactivity measurement is clearly superior in comparison with conductivity measurement. Nevertheless, the combination of the two detection methods is useful for a complete quantitative characterisation of the anion content in the solution, if a calibration with identical buffer and bulk solutions can be done.

Besides iodide and iodate, it is also possible to determine molecular iodine. This is carried out by using pre-filters for molecular and/or organic iodine and following complete reduction with hydrazine solution to the iodide species. At first the iodide and iodate species are detected. After that the filter is eluted with hydrazine containing solution, reducing the remaining elemental iodine to iodide, which then can be detected also on the IC column.

The radioactivity measurement device is suitable for the study of carrier free samples. This is of special interest for investigations of cooling water samples from NPP.

Due to the use of different columns, eluent solutions and iodine stock solutions the peak heights of the several iodine species appear different. Moreover, the iodide/iodate ratio in the chromatogrammes obtained by use of the radioactivity detector is influenced by the composition of the initial spiking ^{131}I -solution. Isotopic exchange can take place very slowly, depending on the special conditions, so that the I^-/IO_3^- ratio detected by the radioactivity detector does not in any case represent the real ratio of inactive iodine species. Real samples from NPPs do not show this effect. Here, all species are in equilibrium. For reliable quantitative results, however, calibration of the system with certified standards is essential.

Concluding remarks

An analytical method was developed to provide the previously missing and important information on the iodine behaviour by determining the concentrations of the common species of iodine in the aqueous phase. If the equipment is completed with the corresponding previous molecular iodine/organo-iodine retaining filters [6], then simultaneous determination of molecular iodine, iodide and iodate can be performed from one sample.

For radioactive samples a CsI(Tl) scintillation detector is used. This gives the possibility to identify iodine species at a non-carrier concentration level and in the presence of impurities, interfering in the conductivity measurement.

To monitor and (specify) contamination in the environment, due to the long-lived iodine fission product ^{129}I , distribution mass separation (of the iodide and iodate fractions after the IC separation) can be performed. The highest sensitivity is achieved by the use of accelerator mass spectrometry (AMS).

The method can be applied to routine analysis of environmental and technical samples with iodine contents from 20 ppb to 50 ppm. However, detailed quantitative determinations using calibrated iodine standards are still necessary for reaching the quality requirements of routine analysis and introduction of the method into industrial application.

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