Separation of Radioiodide, Radioiodate and Radioperiodate by Thin-Layer Chromatography

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A rapid method for the separation of radioiodide, radioiodate and radioperiodate on a thin-layer of silica gel and starch is described. Using the system methanol—25% ammonium hydroxide—water—10% acetic acid (9 : 1 : 1 : 0.5) good separation has been achieved within 45—50 minutes. The method is suitable for the separation of carrier-free radioiodine or radioiodine with a carrier of the concentration up to 10^{-3} M.

Radioiodine may be present in both the technological systems of nuclear reactors and biosphere components in the form of I^-, I^0, I^+, I^{5+} and I^{7+}, respectively, from of which mainly I^-, I^{5+} and I^{7+} should be taken into account [1, 2]. Therefore, radioecological studies of radioiodine formed in uranium fission require a rapid method for the separation of the different chemical forms of iodine especially in the presence of short-lived isotopes of radioiodine.

Attention has been paid to the separation of iodide, iodate and periodate even in the presence of other components (mainly bromine or chlorine anions) using chemically untreated papers and various solvents [3—10], chemically treated papers [6, 9—11] as well as solid ion exchangers [12]. A number of works dealing with the separation of I^-, IO_3^- and IO_4^- were briefly reviewed [13—15]. Recently interest turned towards the separation of halides [16, 17], iodide, iodate and tellurate [18], by thin-layer chromatography.

Experimental

All chemicals and solvents were of anal. grade. $^{131}I^-$ was in the form of carrier-free $Na^{131}I$ (supplied by ÚVVVR, Praha). $^{131}IO_3^-$ was prepared by oxidation of carrier-free $Na^{131}I$ with NaClO in acid medium, $^{131}IO_4^-$ by oxidizing carrier-free $Na^{131}I$ with NaClO in alkaline medium [19].

The model system containing $^{131}I^-$, $^{131}IO_3^-$ and $^{131}IO_4^-$ individually and in mixture, was applied in a volume of 1—5 μl with less than 10^{-10} g of iodine.

Solvent systems based on ethanol—25% NH_4OH—water, acetone—1-butanol—25% NH_4OH—water, methanol—25% NH_4OH—water, methanol—25% NH_4OH—acetic acid—water, acetone—1-butanol—water, ethanol—NaOH, 1-butanol—25% NH_4OH—acetic acid—water, isopropanol—25% NH_4OH—acetic acid—water, *etc.*, in various ratios by volume, were used.

A thin-layer of silica gel, thickness 0.13 mm, with luminescent indicator and a starch binder, type Silufol UV 254 (product of Sklárny Kavalier, Votice, Czechoslovakia) was used. Stripes 20 × 150 mm were cut, or bands 20 mm wide were obtained by removing a width of 2—3 mm of the silica gel layer. Before use, the thin-layer was not treated — neither physically nor chemically.

The chromatograms were developed 40—180 minutes at laboratory temperature, until the solvent front reached the distance of 100—120 mm. The chromatograms were dried at laboratory temperature and the spots were detected either chemically (in the case of ^{127}I in model experiments) as blue spots (with starch in the layer) using the oxidoreduction

$$IO_3^- + 5I^- + 6H^+ \rightleftarrows 3I_2 + 3H_2O,$$
$$IO_4^- + 7I^- + 8H^+ \rightleftarrows 4I_2 + 4H_2O$$

in acid medium or radiometrically by β-counting using a GM counter (window thickness 1.5 mg/cm^2).

Results and Discussion

Using the stable nuclide ^{127}I, a number of solvent systems were selected according to the sharpness and rapidity of separation. In selecting the appropriate solvent system, also form and area of the spots as well as the pH value of the medium were, besides good separation and short development period, the main criteria. In correct separation process alkaline medium with a pH value of 9—10 is required. In both the neutral and acid medium in dependence on pH and mixture composition processes may take place bringing changes of the composition of the sample being separated, *e.g.*

$$IO_3^- + 5I^- + 6H^+ \rightleftarrows 3I_2 + 3H_2O, \quad (A)$$
$$IO_4^- + 7I^- + 8H^+ \rightleftarrows 4I_2 + 4H_2O, \quad (B)$$
$$IO_4^- + 2I^- + 2H^+ \rightleftarrows IO_3^- + I_2 + H_2O, \quad (C)$$
$$IO_3^- + 2I^- + 3H^+ \rightleftarrows 3HIO, \quad (D)$$
$$3I_2 + 3H_2O \rightleftarrows 3HIO + 3H^+ + 3I^-, \quad (E)$$

and the like. When an appropriate solvent was found, the separation was repeated with carrier-free $^{131}I^-$, $^{131}IO_3^-$ and $^{131}IO_4^-$ individually and in mixture.

A good separation is given by solvents based on methanol—25% NH_4OH—water and especially methanol—25% NH_4OH—10% acetic acid—water. The separation of $^{131}I^-$, $^{131}IO_3^-$ and $^{131}IO_4^-$ in the mixture in four chosen solvents is shown in Fig. 1. The composition and development period of these solvents and the R_F values are listed in Table 1. The separation by these solvents proved to be reproducible and reliable, the most satisfactory results being given by the solvent system No. *4* (methanol—25% NH_4OH—water—10% acetic acid, 9 : 1 : 1 : 0.5), where even the development period is the shortest. By means of these solvents the mixture of I^-, IO_3^- and IO_4^- is separated in that way, that I^- moves just behind the solvent front, IO_4^- stays at the origin and IO_3^- moves between iodide and periodate. The position of the spot IO_3^- then depends mainly on the solvent composition.

The change of solvent composition affects mainly the R_F value for IO_3^-, while the changes of the concentrations of NH_4OH, H_2O and CH_3COOH, respectively, do not affect the R_F value for IO_4^- and the influence on the R_F value for I^- is only slight. In following the dependence of the R_F value for iodide and iodate on the concentration of 25% NH_4OH and water in the solvent, the increase of the concentration of

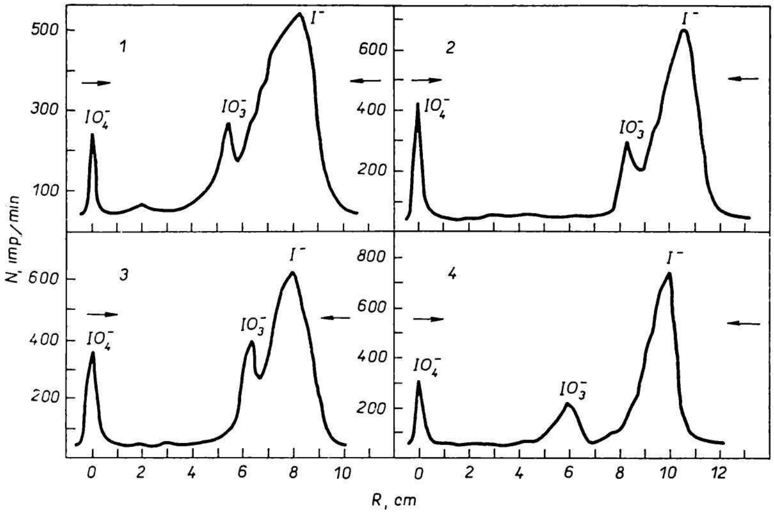

Fig. 1. Separation of $^{131}I^-$, $^{131}IO_3^-$ and $^{131}IO_4^-$ in the solvents No. *1*, *2*, *3* and *4*. The composition of solvents and the R_F values are listed in Table 1.

Table 1

Composition and development period of solvents, and R_F values for I^-, IO_3^- and IO_4^- in these solvents

No.	Solvent: Composition in ratios by volume				Development period for 10 cm chromatograms in minutes	R_F		
	CH_3OH	25% NH_4OH	H_2O	10% CH_3COOH		I^-	IO_3^-	IO_4^-
1	9	1	1	—	66	0.83	0.69	0.00
2	9	1	0.5	—	84	0.85	0.68	0.00
3	9	2	1	—	85	0.85	0.72	0.00
4	9	1	1	0.5	50	0.83	0.51	0.00

both NH_4OH and water has been found to bring about the increase of R_F for iodate, whereas the R_F value for iodide increased but slightly (Figs. 2 and 3). The increase of concentration of acetic acid causes the decrease of the R_F value for iodate and simultaneously the increase of the R_F value for iodide (Fig. 4).

The use of other types of solvents, namely those of higher alcohols causes a rapid impairment of iodate and periodate separation, considerable drop of the R_F value for I^- and also extension of the development period.

The influence of the carrier amount on the separation of $^{131}I^-$, $^{131}IO_3^-$ and $^{131}IO_4^-$ by the solvent No. *4* was studied in the concentration range of 10^{-4}—10^{-1} M. In this range the R_F value for iodide and periodate did not change, whereas it decreased for iodate with concentrations exceeding 10^{-3} M, making the separation of iodate from periodate quite difficult, since the iodate moved with a diffuse tail from the very origin (Fig. 5). Above this concentration the sorbent capacity for the given solvent system and the substance separated is exhausted.

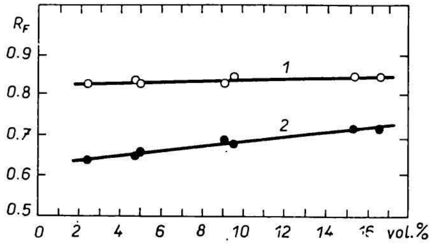

Fig. 2. Influence of the amount (vol. %) of 25% NH_4OH on the R_F values. *1.* I^-; *2.* IO_3^-.

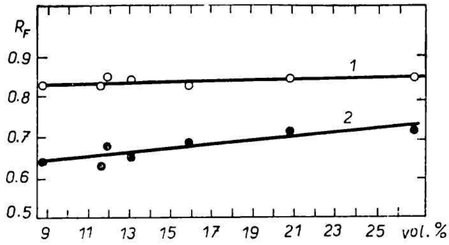

Fig. 3. Influence of the amount (vol. %) of H_2O on the R_F values. *1.* I^-; *2.* IO_3^-.

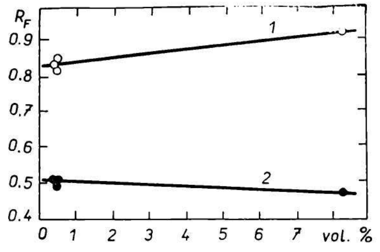

Fig. 4. Influence of the amount (vol. %) of CH_3COOH on the R_F values. *1.* I^-; *2.* IO_3^-.

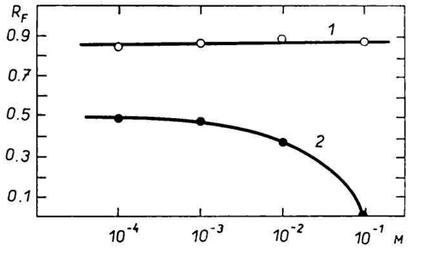

Fig. 5. Influence of the concentration of the carrier $^{127}I^-$ and $^{127}IO_3^-$ on the R_F values. *1.* I^-; *2.* IO_3^-.

The use of thin-layer chromatography in the separation of the different chemical forms of fission isotopes of radioiodine makes it possible to pay attention even to other short-lived radioisotopes of iodine: ^{132}I ($T = 2.28$ h), ^{133}I ($T = 20.8$ h), ^{134}I ($T = 52.8$ m) and ^{135}I ($T = 6.75$ h). The identification of the fission radioisotopes of iodine may be done by gamma spectrometry by the gamma lines 0.364 MeV for ^{131}I, 0.53 MeV for ^{133}I, 0.86 MeV for ^{134}I, 0.96 MeV for ^{132}I, 1.14 and 1.72 MeV for ^{135}I, respectively [20]. The determination of the distribution of ^{136}I ($T = 83$ s) in the different chemical forms would require much quicker separation technique.

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