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Abstract

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Radiation-Kinetic Method for Determining Ultratrace Amounts of Polonium*

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The ability of periodide ions to give bright-colored solid-phase reactions (^{1}), and the lesser ability of iodide ions to do so, can be used for the photometric determination of very small amounts of tetravalent polonium (Po^{210}).

This can be accomplished as a result of a combination of several processes: the process of coprecipitation of polonium, the accelerated local radiolysis of iodides caused by it, the formation of periodide anions, and the color solid-phase reaction of these anions with the cation of butylrhodamine**. It is possible to select such concentrations of iodides and butylrhodamine at which the color solid-phase reaction, caused by the formation of a suspension of the insoluble iodide of the butylrhodamine cation, will proceed only to a slight extent. But to some extent it will proceed, and on the resulting crystals of butylrhodamine iodide, according to the rules of coprecipitation with organic coprecipitants (^{2}), tetravalent polonium will be deposited in the form of butylrhodamine penta- or hexaiodopolonite (^{3}). This local increase in the concentration of polonium on the crystals of butylrhodamine iodide causes enhanced local radiolysis of iodide ions, leading to the formation of elemental iodine and then of periodide. The latter causes the conversion into the insoluble state of new amounts of butylrhodamine and thereby an intensification of the color solid-phase reaction caused by the formation of crystals, now of butylrhodamine periodide. These crystals cause the coprecipitation of additional amounts of polonium, and the process proceeds further, thus constituting a self-accelerating process.

It is important to note that the local increase in the concentration of polonium is accompanied by a simultaneous local increase in the concentration of periodide in the crystals of butylrhodamine periodide. As a result, in the heterogeneous system that forms, radiolysis proceeds more strongly than in a homogeneous system of the same composition. As will be seen below, this is of considerable importance for the sensitivity and especially for the selectivity of the reaction. Thus, owing to this, it proves possible to determine polonium against a background of predominant amounts of certain other α-emitters.

Selectivity of the reaction. Color solid-phase reactions with butylrhodamine in the presence of iodides can be given by all those elements which, under the reaction conditions, are present in solution in the form of heavy, hydrophobic anions. These include both elements, forming iodide anions (Te^IV, Cd, Hg, Bi, Sb, etc.), as well as elements present in other forms, for example as oxygen-containing heavy anions. But these will be ordinary, simple, non-self-accelerating color solid-phase reactions. These same elements may also coprecipitate with butylrhodamine iodide.

If radioactive isotopes of any of the coprecipitating elements are present, and the radiation from these isotopes causes appreciable radiolysis of iodides, then these elements will give the same color self-accelerating reaction as polonium. The sensitivity of the reactions will be determined by the intensity of radiolysis.

Sensitivity of the reaction. The sensitivity of the reaction is the higher, the more time is allowed for radiolysis to proceed, the higher the concentration of the iodide solution in the medium in which the reaction is carried out, and the higher the concentration of butylrhodamine. But if the concentration of the ingredients exceeds a certain, rather low, limit, the blank test will also begin to give a positive reaction, owing to the formation of a suspension of crystals of butylrhodamine iodide.

When the iodide concentration is increased, the reliability of the reaction also decreases owing to the conversion of iodide into periodide under the influence of atmospheric oxygen and light, and of the hydrogen peroxide formed as a result of radiolysis. Radiolysis in the solution caused by the presence of other radioactive elements also increases strongly. Thus, the sensitivity of the reaction and the magnitude of the correction for the blank experiment increase in parallel under the influence of the same factors.

To ensure greater reliability of the reaction, substances that bind elemental iodine should be introduced into the system. They should be introduced at such a selected concentration as would ensure a sufficiently small value of the correction for the blank experiment. Resorcinol is a suitable substance. To increase the sensitivity of the reaction in the system, on the contrary, it is advisable to add a little elemental iodine, in such a concentration that the periodide formed gives an appreciable, but not strong, positive reaction. In this case, crystals of butylrhodamine periodide will be present in the system immediately after the

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* The analytical reaction described in the article is based on a self-accelerating process. At the conference on kinetic methods of analysis (14–16 VI 1960, Ivanovo), where the present work was reported, the name of the analytical reaction of a new type described here was discussed. In practical terms and in its high sensitivity, this new reaction is close to catalytic reactions, while not being such in the strict sense of the term. Perhaps the self-accelerating reaction described should be called a "chain" or "radiation-avalanche" reaction.

** *n*-Butyl ester of rhodamine B. The synthesis was carried out by L. I. Bolshakova.

ingredients are mixed, and the process of coprecipitation of polonium on them will begin at once. In ordinary yellowish, not freshly prepared potassium iodide solution there is always some concentration of periodide, and such a potassium iodide solution gives a very sensitive reaction. Table 1 shows the influence of the factors considered on the sensitivity of the reaction. The concentrations taken were: polonium (Po^210) $2.5 \cdot 10^{-7}$ g/ml, KI $9.6 \cdot 10^{-3}$ M, butylrhodamine chloride $5.5 \cdot 10^{-5}$ M. The activity of the solution was $1.1 \cdot 10^{-6}$ c/l.* Temperature 20°. The result of the reaction is observed 3 min after mixing the ingredients.

The experiments whose results are given in Table 1 were carried out in test tubes with visual evaluation on an imitation scale. This scale, consisting of a set of colored solutions with a smoothly changing color from pink to violet-blue, was prepared as follows:

Test-tube Nos.	1	2	3	4	5	6	7	8	9	10
a	2	1.8	1.6	1.4	1.2	1.0	0.8	0.6	0.4	0.2
b	0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
c	0.015	0.055	0.103	0.148	0.198	0.250	0.300	0.363	0.425	0.468

Note. a –0.001% aqueous solution of safranine; b –0.0014% aqueous solution of methylene blue; c –extinction, measured against water, FEK-M, yellow light filter, 5 mm cuvette.

It is easy to see that, after a 3-minute waiting period, the reaction of polonium at a concentration equal to $2.5 \cdot 10^{-7}$ g/ml gives an entirely distinct positive—reaction. Under the conditions of experiment No. 13 in Table 1, the extinction of the solution, measured against the blank experiment, is 0.235. On an ordinary photocolorimeter one can reliably determine one-fifth to one-seventh of such an extinction value, which will correspond to a polonium concentration of about $5 \cdot 10^{-8}$ γ/ml. These data refer to the isotope Po^{210}, an α-emitter with a half-life of 138 days. For other polonium isotopes the sensitivity of the reaction will, of course, be different.

Table 1

Effect of the presence of elemental iodine on the sensitivity of the reaction in $4.0\,N$ H_2SO_4

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* The polonium concentration was determined by the scintillation method (^5). The measurement error did not exceed ±5%.

No. of experiment	Resorcinol introduced, moles	Iodine introduced, moles	Blank experiment	Experiment with polonium	Difference in units of the arbitrary scale	Conditional sensitivity of the reaction, γ/ml polonium*
1	$2.9 \cdot 10^{-1}$	–	1	1	0	
2	$1.7 \cdot 10^{-1}$	–	1	1	0	
3	$1.5 \cdot 10^{-1}$	–	1	1	0	
4	$8.7 \cdot 10^{-2}$	–	1	1	0	
5	$5.8 \cdot 10^{-2}$	–	1	1	0	
6	$2.9 \cdot 10^{-2}$	–	1	3	2	$1.2 \cdot 10^{-7}$
7	–	–	1	3	2	$1.2 \cdot 10^{-7}$
8	–	$6.4 \cdot 10^{-6}$	1	3	2	$1.2 \cdot 10^{-7}$
9	–	$1.1 \cdot 10^{-5}$	1	3	2	$1.2 \cdot 10^{-7}$
10	–	$2.1 \cdot 10^{-5}$	1	4	3	$8.3 \cdot 10^{-8}$
11	–	$6.3 \cdot 10^{-5}$	1	4	3	$8.3 \cdot 10^{-8}$
12	–	$1.1 \cdot 10^{-4}$	1	4	3	$8.3 \cdot 10^{-8}$
13	–	$2.1 \cdot 10^{-4}$	1	6	5	$5.0 \cdot 10^{-8}$

* Calculated polonium concentration causing a color intensity equal to one unit of the arbitrary scale.

Such high sensitivity is rare even among the most sensitive catalytic reactions. It should be emphasized that even this very high sensitivity is not limiting: the sensitivity can be increased by increasing the time allowed for the reaction to proceed, or by introducing larger amounts of iodine.

Performance of the reaction. We give one of the procedures suitable for the sensitive determination of polonium (Po^{210}) in pure solutions and also in the presence of plutonium-239. The solution under investigation must not contain the elements indicated above, which give colored solid-phase reactions with butylrhodamine.

Before carrying out the reaction, preparation of the solution is necessary, ensuring the presence of polonium in the appropriate ionic form and the removal from polonium solutions of hydrogen peroxide, which is continuously accumulated as a result of radiolysis ([4,6]). The hydrochloric- or nitric-acid solution of polonium under investigation is evaporated to dryness, H_2SO_4 is added, the mixture is heated until sulfuric acid vapors appear, and after cooling it is diluted with water to a concentration of $6N$ H_2SO_4.

Determination of polonium in its pure solutions. To 1.3 ml of the resulting solution with an acidity of $6N$ in H_2SO_4, add 0.37 ml of a freshly prepared

1% potassium iodide solution and 0.1 ml of a 0.01% aqueous solution of elemental iodine, and keep the mixture for 20 min in the dark at 20°. Then add 0.32 ml of a 0.02% aqueous solution of butylrhodamine chloride, and after 5 min assess the color visually against a scale or photometer it. The polonium content is determined from a calibration curve, which is constructed in the same manner by introducing known amounts of polonium into the solution.

Determination of Polonium in the Presence of Plutonium

The procedure is the same, but a calibration curve is used that has been constructed for solutions containing approximately the same amount of plutonium as the solution being analyzed.

If the amount of plutonium in the latter is unknown, one should have a series of calibration curves constructed for solutions with different plutonium concentrations. To an aliquot portion of the solution being analyzed all the ingredients are added except butylrhodamine; the mixture is kept in the dark for 25 min, butylrhodamine is introduced, and the light absorption is determined immediately. The value obtained is regarded as the light absorption of the blank sample. For the work, that calibration curve is chosen for which the light absorption of the zero solution (without polonium) is as close as possible to the value obtained for the blank sample.

Table 2

Photometric determination of polonium on the basis of a radiation-kinetic color solid-phase reaction. Volume of final solution, 2.1 ml

Taken, γ	Taken, γ	Po/Pu	Found Po^{210}	Error, %	Taken, γ	Taken, γ	Po/Pu	Found Po^{210}	Error, %
Po^{210}	Pu^{239}				Po^{210}	Pu^{239}			
$1.1 \cdot 10^{-7}$	–	–	$8.0 \cdot 10^{-8}$	−27	$5.0 \cdot 10^{-9}$	–	–	$6.9 \cdot 10^{-9}$	+40
$8.3 \cdot 10^{-8}$	–	–	$7.1 \cdot 10^{-8}$	−24	$1.1 \cdot 10^{-7}$	$9.8 \cdot 10^{-4}$	1:9000	$1.0 \cdot 10^{-7}$	−8
$7.3 \cdot 10^{-8}$	–	–	$6.4 \cdot 10^{-8}$	−12	$2.2 \cdot 10^{-8}$	$9.8 \cdot 10^{-4}$	1:45000	$2.3 \cdot 10^{-8}$	+4
$6.2 \cdot 10^{-8}$	–	–	$6.3 \cdot 10^{-8}$	+1	$1.7 \cdot 10^{-8}$	$9.8 \cdot 10^{-4}$	1:58000	$1.8 \cdot 10^{-8}$	+6
$5.6 \cdot 10^{-8}$	–	–	$5.5 \cdot 10^{-8}$	−2	$1.1 \cdot 10^{-8}$	$9.8 \cdot 10^{-4}$	1:89000	$1.4 \cdot 10^{-8}$	+27
$9.9 \cdot 10^{-9}$	–	–	$6.2 \cdot 10^{-9}$	−37	$8.6 \cdot 10^{-9}$	$9.8 \cdot 10^{-4}$	1:114000	$1.1 \cdot 10^{-8}$	+27
$8.3 \cdot 10^{-9}$	–	–	$7.6 \cdot 10^{-9}$	−8					

Table 2 gives examples of results obtained in the determination of polonium in pure solutions and against a background of tetravalent plutonium (Pu^{239}). In the last experiment, with $8.6 \cdot 10^{-9}\ \gamma$ of polonium and $9.8 \cdot 10^{-4}\ \gamma$ of plutonium, the activity of the amount of plutonium present, in terms of the number of α-decays per unit time, exceeded the activity of polonium by a factor of 1.6.

The mechanism considered can be used to create highly sensitive radiation-kinetic reactions for other elements as well, the isotopes of which have sufficiently high α-activity, while the ions formed by the elements are capable of coprecipitating with organic coprecipitants.

By the iodide → periodide mechanism, this is possible for all elements forming iodide complex anions. By the nitrate → nitrite → azo-coupling mechanism, this is possible for elements forming stable nitrate complex anions. By the perchlorate → chlorate → readily oxidized organic products mechanism, this is possible for elements capable of coprecipitating with organic perchlorates, i.e., for elements capable of forming ions of the type $MeO_4{}^-$. These and other combinations will be considered in detail in subsequent publications.

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Note: Figure translations are in progress. See original paper for figures.

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