Radioactive Kryptonates in Volumetric Analysis (II) Determination of Calcium by Radiochelatometric Titration

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A method was worked out for the determination of calcium and other cations by titration with radioactive kryptonate of silver iodate AgIO₃[⁸⁵Kr] as end-point indicator. Titration was carried out by the discontinuous method, by measuring the activity of radioactive kryptonate.

The preceding paper [1] dealt in detail with the principles and possibilities of using radioactive kryptonates as indicators in radiochelatometric titrations. The methods of preparation of these substances and the study of their properties from the viewpoint of their analytical application have also been described. The present paper describes the application of this principle in determining calcium.

Into the solution in which calcium is to be determined (similarly Sr^{2+} , Mg^{2+} , etc.) radioactive kryptonate $AgIO_3[^{85}Kr]$ is added and titrated with Chelatone III. After every addition of titrant solution the activity of radioactive kryptonate is measured. This reaction takes place first:

$$Ca^{2+} + [H_2Y]^{2-} \rightleftharpoons [CaY]^{2-} + 2H^+.$$
(A)

After the quantitative binding of Ca^{2+} the excess of Chelatone III reacts with silver ions [2], and dissolves the radioactive kryptonate $AgIO_3[^{85}Kr]$ following this reaction

$$AgIO_{3}[^{85}Kr] + [H_{2}Y]^{2-} \Rightarrow [HAgY]^{2-} + IO_{3}^{-} + H^{+} + ^{85}Kr.$$
 (B)

In consequence, with the addition of titrant solution of Chelatone III there occurs a proportional radioactivity decrease of the kryptonate of silver iodate.

The equilibrium state of reaction (B) is determined by the magnitude $pL_{AgIO_4[^{46}Kr]}$ and the stability constant of the forming compound of silver with Chelatone III. The equilibrium state

$$[HAgY]^{2-} + H^+ \rightleftharpoons [H_2Y]^{2-} + Ag^+ \tag{C}$$

is dependent on pH of solution. The solubility of $AgIO_3$ in Chelatone III is also dependent on pH of solution. According to (B) $AgIO_3$ does not dissolve when pH 5.0, the dissolution begins when pH 5.5 approximately and practically ends when pH 9.5. A more basic medium is not recommended because silver oxide begins to form. The optimum interval pH for carrying out the titration of any ion in agreement with the condition

$$\mathrm{p}K > \mathrm{p}K_{[\mathrm{HAgY}]^2}$$
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ts 9.5-11.5. In this interval the reaction between silver iodate and Chelatone III iakes place quantitatively.

The presence of molybdate, phosphate, tartrate, citrate in great excess do not affect the function of the indicator. On the other hand the titration cannot be carried out in the presence of Cl^- ions.

The discontinuous measuring of radioactivity decrease of kryptonate was carried out in the course of titration.

Experimental

Radiochelatometric indicator

The preparation and properties of radioactive kryptonate of silver iodate $AgIO_{3}[^{85}Kr]$ have been described in paper [1].

Solutions used

 10^{-2} M titrant solution of Chelatone III. The solution was prepared by dissolving an exact amount of compound of p. a. purity in redistilled water. The solution factor was set for calcium carbonate p. a.

Standard solution Ca^{2+} was prepared by dissolving $Ca(NO_3)_2 \cdot 4H_2O$ in redistilled water. The concentration of the solution was determined by chelatometric titration (0.389 mg Ca/ml).

0.1 M solution of sodium hydroxide.

Titration equipment

The schema of the titration equipment is in Fig. 1. The titrated solution is in the titrating vessel θ , which is placed in a double shield case 5 (the inside wall being of poly-



Fig. 1. Schema of titrating equipment for radiochelatometric titration.

1. nitrogen bottle; 2. throttle valve; 3. flow gauge; 4. GM tube; 5. shield case; 6. titrating vessel; 7. burette; 8. measuring gauge; 9. the measuring equipment proper.





methylmethacrylate and the outside wall of lead). GM tube 4 in the measuring gauge 8 is introduced into this case from underneath (to lower the background), which also assures equal geometric detection conditions of radiation in the course of titration. Pulses from GM counter go into the measuring equipment proper 9 (VA-G-20A Mess-platz-Vakutronik). The titrant solution is added by a burette 7. During titration nitrogen from bottle 1 is bubbled through the solution. The flow of nitrogen is controlled by a flow gauge 3 and regulated by a throttle valve 2.

The titrating vessel itself is in Fig. 2. It is a glass tube with a narrowed bottom to assure equal geometric conditions in measuring the activity of radioactive kryptonate. The bottom of the tube is from a thin mica foil a, to lower the absorption of radiation. Nitrogen bubbles through tube b, sealed into the vessel, mixes the solution and carries away the liberated ⁸⁵Kr.

Working process

1-5 ml solution of calcium salt is placed into a titrating vessel, diluted with distilled water to 15 ml and pH of solution is brought to the value 9.00-10.00 by means of 0.1 m of soda lye. Solid radioactive kryptonate AgIO₃[⁸⁵Kr] is added to the solution, which forms an uninterrupted layer at the bottom of the narrowed part of the titrating vessel. The titration begins 10 minutes after the addition of radioactive kryptonate into the titrating medium. During titration nitrogen is bubbled through the solution, which takes away the liberated ⁸⁵Kr. The activity of radioactive kryptonate is always measured 2 minutes after the addition of Chelatone III. The titration curve is plotted from the measured activity values. The activity is expressed in relative units. The activity measured 10 minutes after the addition of radioactive kryptonate into the titration medium is taken to be 100 % (i. e. without addition of Chelatone III).

Results and discussion

Fig. 3 brings for illustration the titration curve obtained in determining 0.778 mg Ca^{2+} titrated with 10^{-2} M titrant solution of Chelatone III. As the titration curve shows, the end-point can be very well evaluated.

In Table 1 the results obtained in titrating 0.778 mg of calcium with 10^{-2} m solution of Chelatone III can be seen. From the Table it can be seen that the repro-

	Am	ount of Ca ²⁺ [mg]	Error		
No.	Added	Determined by radiochelatometric titration	mg	0/ .'0	
1	0.778	0.759	-0.019	-2.45	
2	0.778	0.760	-0.018	-2.36	
3	0.778	0.761	0.017	-2.20	
4	0.778	0.761	0.017	-2.20	
5	0.778	0.757	-0.021	-2.70	
6	0.778	0.765	0.013		
		1	l		

Table 1

Determination of calcium by radiochelatometric titration

duction of determination is good. However, all the deviations of measured values were negative. This would lead to the conclusion that ⁸⁵Kr is liberated just before the end-point. It is in agreement with the results obtained by Lieberman et al. [3] in determining calcium by titration with 0.05 M solution of Chelatone III using solid indicator ^{110m}AgIO₃. It is likely to be caused by close values of stability constants (for chelate: Chelatone III — calcium is pK 10.7; for Chelatone III — silver is pK 7.1), so that silver begins to form chelate even before complete consumption of calcium.



Fig. 3. Titration curve obtained in titrating 0.778 mg Ca^{2+} by 10^{-2} M titrant solution of Chelatone III.

т	a	b	1	e	2
_		_	_	_	_

Determination of calcium by radiochelatometric titration

No.	Am	ount of Ca ²⁺ [mg]	Error	
	Added	Determination by radiochelatometric titration	mg	%
1	0.194	0.189	0.005	2.66
2	0.389	0.370	0.019	5.13
3	0.583	0.571	-0.012	-2.10
4	0.778	0.765	0.013	-1.69
5	0.972	0.955	0.017	-1.70
6	1.166	1.140	-0.026	-2.28

From Table 1 is results that the determination of calcium is marked with a standard deviation $s = \pm 0.0084$ mg. The amount of Ca²⁺ determined by radiochelatometric titration is therefore 0.760 ± 0.0084 mg.

Table 2 gives the results obtained in the titration of various amounts of calcium. By this working process it is also possible to determine other cations, e. g. Sr^{2+} , Mg^{2+} and similarly also calcium in the presence of magnesium. In determining calcium and magnesium in different samples (e. g. in dolomite, in glass, in pharmaceutic preparations etc., as well as in determining the hardness of water) work is done with two aliquot parts of the solution under examination. In one part the total of calcium and magnesium is titrated by the method already mentioned and in the other part after the precipitation of calcium in the form of molybdate, magnesium is titrated (in the filtrate). The amount of calcium is calculated from the difference.

RÁDIOAKTÍVNE KRYPTONÁTY V ODMERNEJ ANALÝZE (II) STANOVENIE VÁPNIKA RÁDIOCHELATOMETRICKOU TITRÁCIOU

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Vypracovala sa metóda na stanovenie vápnika a iných katiónov titráciou odmerným roztokom chelatonu III za použitia rádioaktívneho kryptonátu jodičnanu strieborného $AgIO_3[^{85}Kr]$ ako indikátora bodu ekvivalencie. Po kvantitatívnom viazaní vápenatých iónov nadbytok chelatonu III vstúpi do reakcie so striebornými iónmi a rozpúšťa rádioaktívny kryptonát za uvoľnenia ⁸⁵Kr. V dôsledku toho pridávaním odmerného roztoku úmerne klesá rádioaktivita kryptonátu jodičnanu strieborného. Pri titrácii sa postupovalo diskontinuitnou metódou, meraním aktivity rádioaktívneho kryptonátu. V práci sa opisuje princíp titrácie, skonštruované titračné zariadenie, výsledky získané pri analýze modelových vzoriek vápnika a štúdium reprodukovateľnosti stanovenia.

РАДИОАКТИВНЫЕ КРИПТОНАТЫ В ОБЪЕМНОМ АНАЛИЗЕ (II) ОПРЕДЕЛЕНИЕ КАЛЬЦИЯ РАДИОМЕТРИЧЕСКИМ ТИТРОВАНИЕМ

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Был разработан метод для определения кальция и других катионов титрованием титрованным раствором хелатона III с применением радиоактивного криптоната иодата серебра AgIO₃[⁸⁵Kr] в качестве индикатора эквивалентной точки. После количественного связывания Ca²⁺ избыток хелатона III вступает в реакцию с ионами серебра и растворяет радиоактивный криптонат с выделением ⁸⁵Kr. В результате этого с прибавлением титрованного раствора пропорционально понижается радиоактивность криптоната иодата серебра. Титрование было проведено непрерывным методом с измерением активности радиоактивного криптоната. В работе описывается принцип титрования, построенная титрационная аппаратура, результаты анализа модельных образцов кальция и изучение воспроизводимости определений.

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