RADIOMETRIC TITRATIONS BASED ON THE INTERACTION OF LOW-ENERGY PHOTONS WITH MATTER

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Argentometric titration with the indication of the point of equivalence based on the interaction of low-energy photons with the analyzed matter is described. The characteristic line of silver was excited by the combined source ^{147}Pm/Sm; the samples were either in cuvettes or deposited on the chromatographic paper. The results are — within the limits of experimental errors — — in agreement with the results of the classical argentometric titration with the visual indication of the point of equivalence.

Volumetric determinations are based on chemical reactions in which low-soluble, little dissociated or complex compounds are formed. The predominant part of these determinations comprises methods based on precipitation reactions, among which argentometry and mercurimetry are the most commonly used methods[1]. The lack of a convenient visual or potentiometric indication of the point of equivalence can be removed by the use of radiometric titrations[2]. The radioactivity of the initial component or of the reaction product is measured during the titration and the point of equivalence is given by the intersection of the two branches of the titration curve. The requirement of the separate measurement of the radioactivity of the followed component constitutes the principal condition for the various modifications of the method.

Radiometric titrations based on the interaction of low-energy photons with matter are described in this study. The point of equivalence is indicated by the X-ray fluorescence emitted from the elements present in the volumetric or titrated solutions. The described procedure is compared with the classical argentometric titration according to Mohr[3].

EXPERIMENTAL

The argentometric titration was followed using the characteristic radiation of silver in the titrated solution of silver nitrate (1; 0·1; 0·05; 0·01 mol dm^{-3}). The point of equivalence was determined from the dependence of the measured count rate on the volume of added volumetric solution of potassium chloride. The titration was followed in samples deposited on the chromatographic paper[4] and in samples in cuvettes[5]. The characteristic radiation was excited using a radionuclide beta- and X-rays source ^{147}Pm/Sm (K_{α_1} Sm 40·124 keV, K_{β_1} Sm 45·400 keV, half-life 2·7 years, activity 3·7 . 10^{10} Bq). The energy of this radionuclide source is higher than the absorption edge of silver (25·517 kV) so that it ensures its effective excitation and a perfect resolution

from the K_{α_1} and K_{β_1} lines of silver if a scintillation detector NaI(Tl) (⌀ 25 mm, thickness 2 mm) is used. The angle between the detector axis and the radionuclide source was 50°. The reaction products were separated by centrifugation.

RESULTS

The titration was discontinuous. An aliquot of the titrated solution – 2 ml for samples deposited on the chromatographic paper and 5 ml for samples in cuvettes –

TABLE I

The amount of the volumetric solution (in ml) in the probes

Probe No	Samples on the chromatographic paper KCl, ml	Samples in cuvettes KCl, ml
1	0	0
2	0·5	2·0
3	1·0	3·0
4	1·5	4·0
5	2·0	5·0
6	2·5	6·0
7	3·0	7·0
8	3·5	8·0

TABLE II

Comparison of the results of the titration determination of Ag with the indication of the point of equivalence by the RRFA method and by the method according to Mohr

KCl mol l^{-1}	Determined amount of Ag, g		Relative error ±, %
	visual titration	RRFA titration	
	Paper Whatman 2		
1·0	0·2096	0·2030	3·15
0·1	0·0209	0·0203	2·87
0·05	0·0106	0·0112	5·66
	Cuvette		
1·0	0·5382	0·5382	–
0·1	0·0548	0·0538	1·82
0·05	0·0270	0·0260	3·70
0·01	0·0053	0·0051	3·77

was pipetted into 8 probes and an increasing amount of the volumetric solution was added (Table I). After centrifugation 200 µl of the transparent solution over the precipitate was pipetted on the chromatographic paper, the level of solutions measured in cuvettes was 1 cm. The spectrum of the radionuclide source $^{147}Pm/Sm$ after the interaction with the sample carrier (chromatographic paper), with the Ag sample (200 µl of 1M-$AgNO_3$), with distilled water, and with the 1M-$AgNO_3$ solution is given in Fig. 1. The titration was followed by the measuring of the characteristic line of silver (*i.e.*, in channels No 30–40), the measurement time was 200 s and 40 s (in cuvettes). Fig. 2 presents the dependence of the count rate of the characteristic

TABLE III

The content of chlorides in pharmacenticals permitted by the standard, their titration and RRFA determinations

Preparation batch no	Permitted limits mg/ml	RRFA determination		Mohr titration mg/ml	Relative error ± %
		mg/ml	Standard deviation mg		
NaCl 10% 5 010 677	95–105	103·0	0·13	104·1	1·05
NaCl 10% 020 877	95–105	105·5	0·30	101·8	3·63
NaCl 0·9% 291 276	8·5–9·5	9·4	0·01	9·1	3·29
$CaCl_2$ 10% 5 021 275	95–105	101·5	0·26	98·3	2·24
$CaCl_2$ 10% 260 277	95–105	104·6	0·05	101·4	3·15
	mg/tbl	mg/tbl	mg	mg/tbl	± %
KCl tbl. 2 170 477	475–525	512·7	0·58	481·0	6·59
KCl tbl. 2 210 678	475–525	488·8	0·69	485·0	0·78
KCl tbl. 2 110 977	475–525	524·7	0·49	496·0	5·79

radiation on the amount of the added volumetric solution of 0·1M-KCl ($I = f(V)$; I – the measured rate corresponding to the characteristic radiation of Ag, V – ml). The intersection of the two branches of the titration curve gives the point of equivalence on the abscissa. The reliability of the described titration method was evaluated using the relative error, given by the difference between the amount of silver determined by the titration with the visual indication of the point of equivalence and with the indication using the characteristic radiation of silver (Table II).

The described method of the indication of the point of equivalence using the characteristic radiation of the element (Ag) present in the volumetric or titrated solution was used for the determination of chlorides in pharmaceuticals – 10% and 0·9% NaCl injections, 1% $CaCl_2$ injections and KCl tablets. The permitted amounts of chlorides (in mg/ml) given by the technical standards, the values obtained by the described method together with the corresponding standard deviation, and the values obtained by the argentometric titration are summarized in Table III.

The worked out method for the determination of the point of equivalence and for following the titration is objective, it is based on the interaction of low-energy photons with the atoms of elements in the volumetric or titrated solutions. It can be performed after the separation of the precipitate directly in the cuvettes or on an appropriate carrier if working with small volumes (down to 20 µl). The advantage in comparison with the radiometric titration in which radioactive indicators are

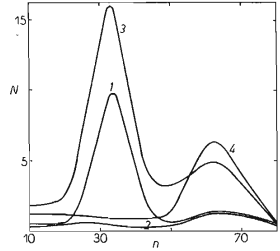

FIG. 1

Spectrum of the radionuclide source $^{147}Pm/Sm$. Interaction: *1* 200 µl 1M-$AgNO_3$ on a carrier; *2* sample carrier (Whatman 2); *3* 1M-$AgNO_3$ in a cuvette; *4* distilled H_2O in a cuvette. Count rate N . 10^3; time of measurement 10 s; *n* channel number

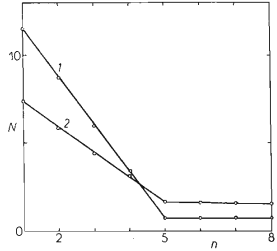

FIG. 2

Titration curves. *1* Samples deposited on a chromatographic paper; count rate N . 10^4, time of measurement 200 s; *2* samples in cuvettes; count rate N . 10^5; time of measurement 40 s; *n* probe number

used is given by dealing with inactive titrated and volumetric solutions. From the titration curves it follows that there is still another advantage of this method – a low number of measurements for the determination of the point of equivalence.

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