TITRATION OF SULPHATES AND LEAD USING LEAD ION SELECTIVE ELECTRODE

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Titration of sulphates with lead perchlorate employing lead ion selective electrode indication was studied using additions of various organic solvents at different pH' and ionic strength values. As the optimum emerged systems with 60—70% 1,4-dioxane, pH' 5·3—5·6. After dehydration with sodium hydroxide, dioxane must be freed from the electrode surface-oxidizing impurities by their reduction with sodium metal and subsequent distillation. The method was applied to determination of sulphates in mountain spring waters. Units of ppm can be determined; the limit of determination, however, depends considerably on the content of dioxane, total salt content in the sample, and speed of the semi-automatic titration. Lead can be determined with EDTA in concentrations down to $c(\text{Pb}^{2+}) = 5 \cdot 10^{-6}$ mol l^{-1}.

Environmental control, study of atmospheric circulations, and hydrogeochemical prospecting are fields of activity in which determination of sulphates becomes matter of concern. At present, sulphates are determined titrimetrically using visual indication of the end point[1,2], turbidimetrically[3], spectrophotometrically[4], and increasingly also by titrations based on precipitation reactions using lead[5-12] or barium[13,14] ion selective electrode indication. While precipitation of barium sulphate is more selective, lead sulphate can be obtained from aqueous solutions in purer form as crystalline precipitate. Since the solubility of lead sulphate in water is rather high ($pK_s = 7.97$ at 18°C, ref.[15]), organic solvents suppressing the solubility are added to the solutions to be titrated. Addition of 50% dioxane[6] lowers the solubility of lead sulphate considerably, but the peroxidic substances formed on its decomposition oxidize the Pb-ISE rapidly[8,16]. For this reason, alternative systems – 70–75% methyl alcohol[8,12] or 80% isopropyl alcohol[10] – are nowadays preferred.

The main objective of this work was semi-automatic determination of sulphates in mineral natural waters. In addition, chelatometric titration of lead with EDTA using lead ion selective electrode was dealt with too.

EXPERIMENTAL

Apparatus

An RTS 622 titration apparatus comprising a PHM 64 pH/mV-meter, REC 61/REA 160 recorder, TTA 60 titrator, and ABU 13 autoburette with a 2·5 ml burette was used. During the sulphate determination, the pH was held contant by employing a one-sided pH-stat composed of a PHM 62 pH/mV-meter, an additional TTA 60 titrator, and an ABU 12 autoburette. All the instruments were products of Radiometer, Copenhagen.

Crytur 82—17 (Monokrystaly, Turnov) and Orion 97—82A (Orion, U.S.A.) lead ion selective electrodes, a GK 2301 C glass electrode and a K 401 saturated calomel electrode (both Radiometer, Copenhagen) connected by an external bridge containing 3M-$NaNO_3$ were used.

Chemicals

0·01M solution of lead perchlorate was prepared from $Pb(ClO_4)_2.3\,H_2O$ (Smith Chemical Co., U.S.A.) and standardized chelatometrically with 0·05M-EDTA using xylenol orange as the indicator. A $5\,.\,10^{-3}$M titrant solution was used for the titrations. The EDTA solution was obtained by dissolving a weighed portion of the dried chemical, and standardized with zinc nitrate using xylenol orange as the indicator. The sulphate standard solutions were obtained by diluting a 0·1M-Na_2SO_4 stock solution prepared by dissolving anhydrous sodium sulphate *p.a.* (Lachema). Methyl alcohol, isopropyl alcohol, and acetone *p.a.* (Lachema) were purified by distillation; 1,4-dioxane was dehydrated with sodium hydroxide prior to the distillation and after 24 h water residues and oxidizing products of dioxane decomposition were removed with sodium metal and the dioxane was distilled.

All concentrations reported in this paper only refer to the aqueous phase of the solution titrated. During the pH measurements, the effect of dioxane was ignored, the standardization relied on aqueous buffers; this is expressed by denoting the values measured as pH′.

Working Procedure

The lead ion selective electrodes were daily or after each longer pause ground with wet grinding powder on a fabric and three times dipped for several seconds into a $5\,.\,10^{-3}$M-$Pb(ClO_4)_2$ solution; between the expositions, the electrodes were rinsed with distilled water. For the titrations of sulphates in the total solution volume of 50 ml (usually, 20 ml of the sample and 30 ml of dioxane), the pH′ value was adjusted to 5·5 by adding 0·1M-NaOH under pH-static control. The titrant flow rate during the titration did not exceed 0·25 ml/min. The total titrant consumption being typically about 0·8 ml, the titration took approximately 5 min. The titration end point was determined as the centre of the line segment substituting the titration curve in the region of the highest potential change (Fig. 2).

RESULTS

Titration of Sulphates with Lead Perchlorate

As preliminary experiments indicated, addition of commercial reagent grade isopropyl alcohol or, notably, dioxane to the solution to be titrated brings about shift of the potential of the Pb-ISE in the positive direction, as though the $a_{Pb^{2+}}$ value increased gradually, and the electrode potential after exposition to such a mixed solution is irreproducible. For this reason, the organic solvents were first purified by distillation and dioxane was freed from water and peroxides as mentioned above.

The effect of organic solvents on the titration curves was compared for solutions containing 60% methyl alcohol, isopropyl alcohol, acetone, and dioxane, respectively. As demonstrated by Fig. 1, the highest potential jump in the equivalence point range is attained in the dioxane system (pK_s ~ 12), the lowest effect appears in the methyl alcohol system; the potential jump for 60% dioxane was twice as high as in 60% methyl alcohol.

The magnitude of the potential jump in the equivalence point range and thus the minimum determinable quantity of sulphates depend, however, also on other factors affecting the solubility of lead sulphate in the solution titrated, notably the proportion of the nonaqueous solvent in the system and the pH and ionic strength

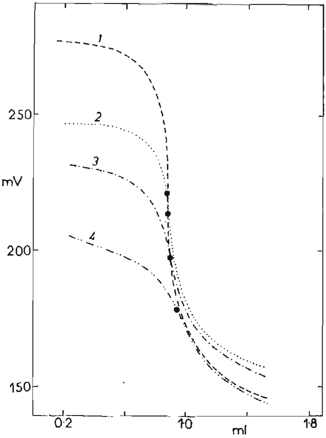

FIG. 1

Effect of Organic Solvents on the Titration of Sulphates with Lead Perchlorate

Solution of 20 mg SO_4^{2-}/l titrated with $5 \cdot 10^{-3}$M-$Pb(ClO_4)_2$ at pH' 5·5, 60% organic solvent: *1* dioxane, *2* acetone, *3* isopropyl alcohol, *4* methyl alcohol.

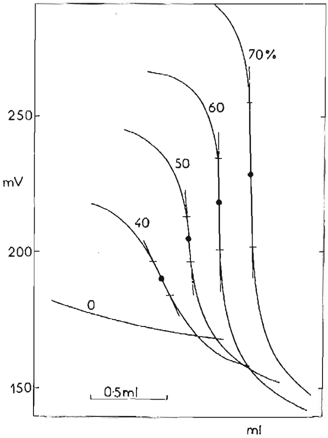

FIG. 2

Effect of Dioxane Concentration on the Titration of Sulphates with Lead Perchlorate

Solution of 20 mg SO_4^{2-}/l titrated with $5 \cdot 10^{-3}$M-$Pb(ClO_4)_2$ at pH' 5·5, *I* approximately $6 \cdot 10^{-4}$; the curves are mutually shifted by 0·2 ml on the *x*-axis. The figure illustrates the way of reading the consumption from the titration curves, ● denotes the titration end point.

values. As expected, the potential jump in the equivalence point region rises rapidly with the increasing content of dioxane (Fig. 2). The effect of pH' is less straightforward (Fig. 3). The best deveoped curves for 60% dioxane solutions were obtained for pH' approximately 5·3–5·6; beyond this range, the usable potential difference diminishes. Moreover, at higher pH' the consumption of the titrant increases (Fig. 3, curve 6), probably on account of formation of basic lead salts. A growing ionic strength of the solution titrated also lowers the potential jump dramatically (Fig. 4). When the pH-stat is employed for the pH' adjustment, and thus only the really necessary volumes of 0·1M-NaOH are added, the increase in the ionic strength during the pH' adjustment is minimal and the titration curves are best developed. If the pH' before the titration exceeds 5·5, the solution should be acidified with a drop of, *e.g.*, 0·1M-HNO_3.

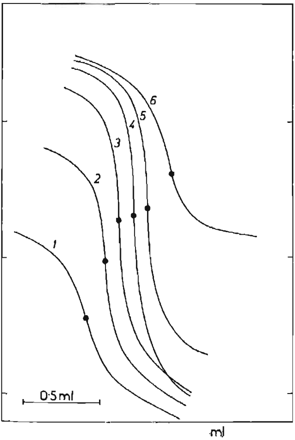

FIG. 3

Effect of pH' on the Titration of Sulphates with Lead Perchlorate

Solution of 20 mg SO_4^{2-}/l in 60% dioxane titrated with 5 . 10^{-3}M-$Pb(ClO_4)_2$. The titration curves are mutually shifted by 0·1 ml on the *x*-axis. pH': *1* 3, *2* 4, *3* 5·3, *4* 5·6, *5* 6, *6* 7.

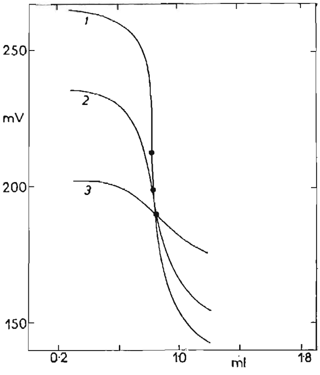

FIG. 4

Effect of Ionic Strength on the Titration of Sulphates with Lead Perchlorate

Solution of 19·2 mg SO_4^{2-}l in 60% dioxane titrated with 5 . 10^{-3}M-$Pb(ClO_4)_2$ at pH' 5·5, the ionic strength adjusted with sodium nitrate. *I*: *1* 6 . 10^{-4}, *2* 0·01, *3* 0·1.

The sulphate concentrations were determined by two independent methods: the titrimetric method under study and a spectrophotometric method based on precipitation of barium sulphate in a dioxane-containing solution using excess Ba^{2+} solution, and photometric determination of the excess barium in a complex with thorine[4]. The titrimetric method gave on average higher results than the spectrophotometric method for both standard solutions and natural water samples (Table I). Five parallel titrimetric determinations of the standard of 19·2 mg SO_4^{2-}/1 gave the average relative error +1·51% and relative standard deviation $s_r = 0·83\%$. With the spectrophotometric method, the relative error +0·73% was obtained for the same solution. The average difference between the titrimetric and spectrophotometric determinations of natural water samples with $c(SO_4^{2-}) > 8$ mg/l was 1·41%; considerably higher results as compared with the spectrophotometric method were

TABLE I

Results of Titrimetric and Spectrophotometric Determination of Sulphates

Titrant solution: $5 . 10^{-3}$M-$Pb(ClO_4)_2$, the solution titrated contained 0·3 mg La^{3+}/l.

Sulphate ions found mg/l		Difference %
Titrimetrically	Spectrophotometrically	
10·2[a]	10·0	+ 2·0
14·3	14·5	— 1·4
18·6[b]	17·8	+ 4·5
18·2	17·8	+ 2·2
18·7	18·3	+ 2·2
15·4	14·7	+ 4·8
13·4	14·8	— 9·5
7·7	6·8	+13·2
14·7	13·8	+ 6·5
15·2	15·7	— 3·2
14·2	15·8	—10·1
10·7	9·7	+10·3
12·7	11·6	+ 9·5
12·4	12·1	+ 2·5
7·1	5·4	+31·5
9·4	7·3	+28·8
14·3	14·3	0·0

[a] Standard solution of 10 mg SO_4^{2-}/l; [b] in the absence of lanthanum nitrate.

found titrimetrically for contents $c(SO_4^{2-}) < 8$ mg/l, where the equilibrium does not establish rapidly enough, so that overtitration takes place during the semi-automatic titration.

In any precipitation titration in complex solutions, coprecipitation or scavenging of other low soluble compounds is a complicating factor. Titration of sulphates with a lead salt may be accompanied by coprecipitation of lead phosphate and, at higher concentrations, of lead fluorides, chlorides, and hydrogencarbonates; coprecipitation of calcium sulphate has to be taken into account too. A 100-fold excess of chlorides does not interfere with titration of 20 mg SO_4^{2-}/l, the titration curve, however, is considerably flatter and resembles, *e.g.*, curves *3* in Fig. 4. Fluorides do not interfere even in the maximum expected concentration in waters, *i.e.* 2·5 mg F^-/l; a mixture of 2·5 mg F^-/l with 50 mg Cl^-/l does not affect the determination either. At $p\underline{H}'$ 5·5, no effect was exerted by HCO_3^- in amounts of 25 mg/l. Phosphates, on the other hand, affected the results appreciably; in the presence of 2·5 mg HPO_4^{2-}/l, the error of determination of 20 mg SO_4^{2-}/l was +16·5%, and in the presence of 18 mg HPO_4^{2-}/l the error was as high as +72%. Addition of lanthanum nitrate has been recommended[17] for $c(PO_4^{3-}) > 2$ mg/l. When the addition is such that the final concentration of La^{3+} is 0·3 mg/l, the results of determination of the standard are lowered by approximately 2–3% and the positive error of determination of sulphates in the presence of 2·5 mg HPO_4^{2-}/l is reduced by approximately 9%. Such additions of La^{3+} were applied even though the concentration of phosphates in the water samples was below 1 mg/l, in order to reduce the positive error of titration and to suppress the effect of phosphates in trace concentrations. Calcium in the natural waters analyzed, present in concentrations 4–7 mg/l, did not affect the determination appreciably.

Titration of Lead with EDTA

During the chelatometric titration of lead with EDTA, the equilibrium establishes considerably faster than during the precipitation titration of sulphates with a Pb^{2+} solution. The *E*-pH plots (Pourbaix-Reilley diagrams – see Figs 5*a* and 5*b*) evidence that at pH 5–5·5, solutions of $2{\cdot}5 \,.\, 10^{-5}\text{M-}Pb^{2+}$ can be reliably titrated. The behaviour of the two electrodes, however, is different: in comparison with the Orion electrode, the potential of the Crytur electrode is less dependent on the pH in the acidic region (Fig. 5a), whereas in the alkaline region the electrode is more liable to oxidation. The usable potential jump in titrations of lead with EDTA was considerably lower for the Orion electrode (Fig. 5*b*).

Since hydroxonium ions are generated during chelatometric titrations, the solutions should be generally adequately buffered. Titrations of lead, however, do not strictly require use of a pH-stat, the weakly acidic solution may be adjusted to the desired value, *e.g.*, with additions of 0·02M hexamethylenetetramine prior titrated to pH 5·8. On the other hand, if the lead titrated is present in low concentrations, it is advisable to check the solution for impurities. The content of metal impurities in hexamethylenetetramine can be reduced, for instance, by extraction with saturated solution of dithizone in tetrachloromethane or trichloromethane[18]. The average relative error of titration of 20 ml of $2{\cdot}5 \,.\, 10^{-5}$M-Pb^{2+} solution with $5 \,.\, 10^{-4}$M-EDTA was $+0{\cdot}14\%$, the relative standard deviation was $s_r = 0{\cdot}71\%$ $(n = 5)$. The error was as high as $+7\%$ and even $+28\%$ when the lead concentration was lowered to $4{\cdot}6 \,.\, 10^{-6}$ and $2{\cdot}3 \,.\, 10^{-6}$ mol/l, respectively.

DISCUSSION

Lead ion selective electrodes involving PbS–Ag_2S mixtures are liable to surface oxidation[5,19], lead oxide or the more soluble lead sulphate or dioxide probably forming on the membrane surface. The surface oxidation brings about poor repro-

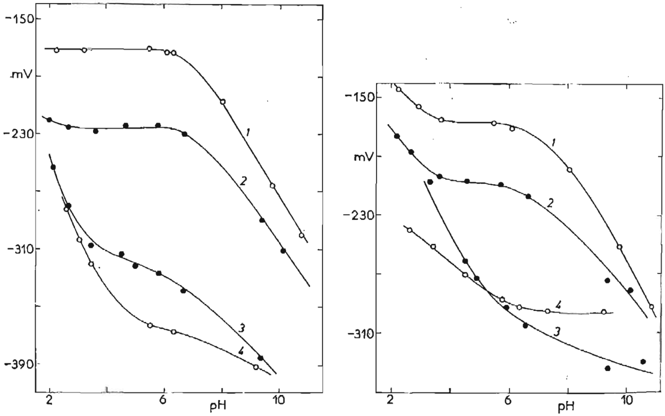

FIG. 5

E — pH Diagrams

a Crytur 82—17 electrode, *b* Orion 97—92A electrode. The pH was adjusted with small additions of 1M-HNO_3 and 1M-NaOH, the ionic strength was not adjusted. Concentration of lead perchlorate (mol l^{-1}): *1* $2{\cdot}5 \,.\, 10^{-3}$, *2* $2 \,.\, 10^{-5}$, *3* $2 \,.\, 10^{-5}$, *4* $2{\cdot}5 \,.\,.\, 10^{-3}$. n(EDTA)/n(Pb) (n is the mass amount): *1* 0·5, *3* 0·5, *3* 1·5, *4* 1·5.

ducibility of the electrode potential; mainly for this reason these ISE's have been employed in direct potentiometry only exceptionally. Lead sulphide is not a perfectly stable compound and its tendency to oxidation in the presence of oxygen rises with growing pH of the solution[20]. Relatively more stable is silver sulphide; this may be one of the reasons why Pb-ISE membranes with its admixture exhibit a steadier and better reproducible response than those containing the lead chalcogenide solely[21]. The membrane oxidation is obviously a surface phenomenon, since the original properties of the electrode restore after a short grinding of its surface.

In solutions containing organic solvents, the electrode surface may be, in addition, oxidized by impurities or products of their decomposition. The potential stability and reproducibility of the titration curves can be, however, improved considerably by a simple purification of the solvents. This makes it possible to employ 1,4-dioxane in titration of sulphates; to our knowledge, this solvent is most efficient in suppressing the solubility of lead sulphate.

The system of 60% dioxane can be recommended for titration of sulphates. When the dioxane is added in higher proportion, the limit of determination is further lowered, but this advantage is offset by the increased hazard of precipitation or coprecipitation of other low soluble substances, such as calcium sulphate[8,12], provided that the conditions are suitable. Thus 70% dioxane can be used with advantage for analysis of rain water and snow samples, with very low total salt contents.

The relative error of determination for the precipitation titration of sulphates with Pb^{2+} solution is slightly positive at $c(SO_4^{2-}) > 10^{-4}$ mol/l, most probably owing to a delay in the indicating electrode response. Any factors affecting the electrode response, such as oxidized surface, stirring speed, or rate of addition of the titrant, affect thus the error of titration. On the whole, however, the agreement between the two methods applied in this work is very good for these concentrations. At $c(SO_4^{2-}) < 10^{-4}$ mol/l a very slow course of titration must be chosen with regard to the possible overtitration.

Serious interference may be caused by phosphates; they have to be removed in advance if present in the solutions in higher quantities[22,23]. Another shortcoming is the pronounced dependence of the potential of the equivalence point on the ionic strength; as a consequence, titrations of sulphates can be carried to the end point or potential, determined in advance, only under favourable conditions, *i.e.* in waters with low contents of salts and higher contents of sulphates.

The chelatometric titration method enables rather highly dilute lead solutions to be analyzed, and thus in some cases can replace direct potentiometric determination of Pb^{2+}. At $c(Pb^{2+}) < 1 \,.\, 10^{-5}$ mol/l, positive titration errors appear, due to an insufficient rate of establishment of the potential in such dilute solutions. Moreover, additions of a buffer may affect the titration infavourably because of the presence of impurities in the buffer solution. Determination of lead in concentrations exceeding $1 \,.\, 10^{-5}$ mol/l is accurate, but not very selective, as the complex of lead with EDTA is only among moderately stable metal–EDTA complexes, $pK_{ML} = -18{\cdot}0$ (20°C, I 0·1) (ref.[24]).

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