Interference Study on a Continuous-flow Determination System for Sulphate With a Lead-selective Electrode Detector and its Application to Natural Water Analysis

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In the continuous-flow determination of sulphate with a lead(II) nitrate reagent solution by using a lead-selective electrode as a potentiometric detector, the interference from hydrogen carbonate, chloride, calcium, nitrate and phosphate was examined in various compositions of the reagent solution. Positive interference from hydrogen carbonate was observed even in the presence of an acidic buffer. An anomalous concentration-dependent chloride interference was interpreted in relation to the dynamic response of the lead-selective electrode in the presence of chloride. The optimised composition of the reagent solution is 1×10^{-5} or 5×10^{-5} M lead nitrate - 1×10^{-3} M monochloroacetic acid - 1×10^{-2} M sodium perchlorate in ethanol for rain and river water analysis, respectively. At the optimum lead ion concentration, continuous determination of sulphate in river and rain water was successfully carried out.

Keywords: *Lead-selective electrode; sulphate determination; continuous-flow analysis; water analysis; interference study*

Although sulphate is one of the major components of natural waters, its determination is of particular importance with respect to the problems of air and water pollution and to acid rain. However, a widely acceptable method for sulphate determination is still not available, especially with respect to continuous analysis.

A lead-selective electrode has been used as an indicator electrode for the potentiometric titration of sulphate.[1-3] A continuous-flow analysis system using two lead-selective electrodes has been reported.[4] The flow injection system developed by Coetzee and Gardner[5] using a flow-through lead electrode modified to a continuous-flow analysis system, and a new calibration procedure, based on the ionic equilibrium between sulphate and lead(II) in a methanol - water mixture, has been proposed by Hara *et al.*[6] In this system, only three calibration points are needed in order to obtain the whole calibration graph for the concentration range 1×10^{-5}–1×10^{-3} M sulphate.

This paper describes the results of a further study for the purpose of applying this system to natural water analysis. The interference from five inorganic ions was examined in lead(II) solutions of various composition. The factors examined were acidity, lead ion concentration, ionic strength and water content of the reagent solution. The dynamic response of a lead-selective electrode in the presence of interfering ions was also examined as a preliminary study. Analysis of discrete river water samples and continuous analysis of river and rain water samples were carried out using this system.

Experimental

Apparatus

An Orion 94-82 lead(II)-selective electrode was used together with a double-junction type reference electrode (Radelkis OP821P or Orion 90-02-00). The outer filling solution was 1 M sodium nitrate. The electrode potentials, at room temperature (24 ± 1 °C), were measured with a precision of 0.1 mV using an Orion 701A digital pH/mV meter and were recorded with an analogue pen recorder (Rikadenki R-11) and also transmitted every 0.6 s to an NEC PC8801 MkII microcomputer through an 8-bit parallel interface.

A schematic diagram of the continuous-flow analysis system is given in a previous paper.[6] Peristaltic pumps (Atto Models 1221H and 1220) were used to deliver the reagent and sample and to pump the two waste solutions from the de-bubbler and

flow cell. The flow-rates of the reagent, sample, de-bubbler and waste from the flow cell were adjusted to *ca.* 2.5, 1.0, 0.9 and 5 ml min^{-1}, respectively. The sample and reagent solutions were mixed in a mixing chamber (6 × 7 mm i.d.) containing a mixing coil (2.3 m × 1 mm i.d.). A wall-jet type flow cell made of transparent acrylic resin (6 cm long, 7 cm high and 4 cm wide) was employed.

Reagents

The reagent solution was composed of lead nitrate, sodium perchlorate as an ionic strength adjuster and a pH adjuster such as monochloroacetic acid dissolved in distilled ethanol. The concentration of lead(II) was determined by potentiometric titration using a standard sodium sulphate solution beforehand. The acidity and specific conductivity of the solution collected from the waste line were measured for every experiment. As the waste solution was *ca.* 70% v/v ethanolic solution, the direct reading of a pH meter was taken as a measure of acidity and expressed as pH'. (The pH is defined only in aqueous solutions. The pH' values obtained here may be different from the pH to some extent because of the addition of ethanol.) Analytical-reagent grade reagents and distilled water were used for all the experiments.

Calibration Procedure

The calibration procedure for the continuous-flow system was as described in a previous paper.[6] Only the conclusion from the calculation of the precipitation equilibrium between lead and sulphate is shown below.

The relationship between the electrode potential of a lead-selective electrode and the sulphate concentration of a sample solution is given by combining the following Nernstian equation:

$$E = E_0 + S\log [\text{Pb}^{2+}]_{\text{free}} \qquad \cdots \qquad \cdots \quad (1)$$

with the equation on the free lead(II) ion concentration,[5,6]

$$[\text{Pb}^{2+}]_{\text{free}} = 0.5 \, (mc^0{}_{\text{Pb}} - dc^0{}_{\text{SO}_4}) + [(mc^0{}_{\text{Pb}} + dc^0{}_{\text{SO}_4})^2 - 4 \, (mc^0{}_{\text{Pb}} dc^0{}_{\text{SO}_4} - K_{\text{sp}})]^{\frac{1}{2}}) \quad (2)$$

where m is the mixing ratio, d the dilution factor, $c^0{}_{\text{Pb}}$ the concentration of lead(II) in the reagent solution, $c^0{}_{\text{SO}_4}$ the concentration of sulphate in the sample solution and K_{sp} the solubility product of lead sulphate. The mixing ratio m and the

dilution factor d can be calculated from the flow-rate of reagent (f_r) and sample (f_s) solutions as $m = f_r/(f_r + f_s)$ and $d = f_s/(f_r + f_s)$, respectively. The volume change was estimated to be 3% after mixing an aqueous sample solution with the ethanolic reagent solution and this value was taken into account in the calculation process when using the microcomputer. The unknown parameters are the standard electrode potential E_0, slope S and the solubility product K_{sp}. With three standard solutions, E_0 and S can be eliminated from equation (1), giving the following ratio:

$$\frac{E_1 - E_2}{E_2 - E_3} = \frac{\log([Pb^{2+}]_1/[Pb^{2+}]_2)}{\log([Pb^{2+}]_2/[Pb^{2+}]_3)} \quad .. \quad .. \quad (3)$$

In equation (3), only K_{sp} is an unknown parameter and can be obtained by solving this equation numerically.[6] Hence, the other two parameters, E_0 and S, can be obtained using the determined value of K_{sp}.

The unknown sulphate concentration can be found from the following equation:

$$E_{st} - E_{sample} = S\log([Pb^{2+}]_{st}/[Pb^{2+}]_{sample}) \quad .. \quad (4)$$

where $[Pb^{2+}]_{st}$ and $[Pb^{2+}]_{sample}$ are given by equation (2) with the standard and sample sulphate concentrations substituted for $c^0_{SO_4}$. A sample solution and one of the standard solutions were measured alternately and the measured potential of the sample was corrected using the measured potential of the standard in order to compensate for the possible drift in potential of the lead-selective electrode.

Evaluation of Interference

The relative error in the determination of 1×10^{-4} M sulphate in the presence of interfering ions was determined from the apparent concentration calculated from the observed potential. The concentrations of interferents are determined as the expected maximum concentration level in river waters of Shiga prefecture, *i.e.*, 1×10^{-3} M for hydrogen carbonate, 5×10^{-4} M for chloride, nitrate and calcium and 1×10^{-5} M for phosphate.

Analysis of River Water

For the purpose of comparison, turbidimetric determination of sulphate in natural waters was carried out after filtration of samples with a Millipore HAWP 04700 filter. The reagent solution for turbidimetry was composed of 30 ml of concentrated hydrochloric acid, 75 g of sodium chloride, 50 ml of glycerin in an ethanol - water mixture (100 + 300 ml). A 3-ml volume of the reagent solution, followed by 5 ml of barium chloride (120 g l^{-1}) were added to the sample solution. The absorbance was measured at 460 nm after agitating for 3 min using a magnetic stirrer.

The determination of other components was carried out according to the following methods.[7] Calcium was determined by complexometric titration with ethylenediaminetetraacetic acid (EDTA). Alkalinity (pH 4.8) was determined by acid - base titration with sulphuric acid as titrant. Chloride was determined by argentimetric titration with a silver-selective electrode as the indicator electrode. Phosphate was determined by spectrophotometry using the Molybdenum Blue method.

Analysis of Rain Water

Rain water was collected with a large funnel, diameter 30 cm.

Dynamic Response

Two experiments were carried out in order to obtain the potential - time response curve of the lead-selective electrode in the presence of an interfering ion. The experimental

technique used here is defined as an injection method,[8] because a concentrated solution in a small volume is injected by means of a syringe into the rapidly stirred test solution, in which the lead-selective electrode has been previously equilibrated. A 50-ml portion of the reagent solution of standard composition $(1 \times 10^{-5}$ M $Pb(NO_3)_2 - 1 \times 10^{-3}$ M $CH_2ClCOOH - 1 \times 10^{-2}$ M $NaClO_4$ in 98.8% v/v ethanol) was mixed with 20 ml of distilled water. This solution was used as the base solution.

In the first experiment, after equilibration of the lead-selective electrode in the base solution, 0.1 ml of a solution containing one of the following interferents was added: (i) 0.02 M Na_2SO_4; (ii) 0.2 M $NaHCO_3$; (iii) 0.1 M NaCl; and (iv) 0.002 M KH_2PO_4. The potential change was then recorded with the analogue pen recorder.

In the second experiment, after equilibration of the lead-selective electrode in the base solution, 0.1 ml of 2×10^{-2} M Na_2SO_4 was added. When a stable potential had been achieved, 0.1 ml of a solution containing the interferent was added [0.2 M $NaHCO_3$; 0.1 M NaCl; 0.002 M KH_2PO_4; or 0.1 M $Ca(NO_3)_2$] and the potential change recorded.

Results and Discussion

Response to Sulphate

Calibration graphs

Fig. 1 shows the calibration graphs obtained with five different concentrations of lead reagent. The non-linearity of the calibration graphs reflects the titrimetric character of the system. The theoretical calculation with only three points reproduces the S-shaped curves fairly well. The sensitivity to sulphate between 1×10^{-4} and 1×10^{-5} M decreases with an increase in lead concentration. For rain water analysis, the graph of line 1 is used as a calibration graph because the sensitivity at *ca.* 1×10^{-5} M is important, while the graph of line 4 is used for the analysis of river water because the concentration of sulphate in river waters is usually *ca.* 1×10^{-4} M.

Accuracy and precision

Table 1 gives the results of five replicate measurements of five different sulphate samples in order of increasing concentration, with two reagent solutions having different lead ion concentrations $(1 \times 10^{-5}$ and 5×10^{-5} M). The relative standard deviation (RSD) was within 5.7%. The error may sometimes exceed 10% with certain concentrations of
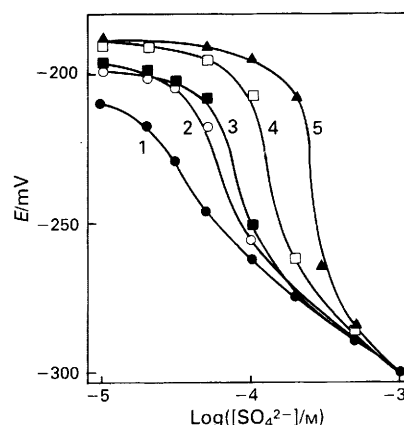

Fig. 1. Calibration graphs for sulphate. Reagents: sodium perchlorate, 1×10^{-2} M; monochloroacetic acid, 1×10^{-3} M. Lead nitrate: 1, 10.6×10^{-6}; 2, 20.5×10^{-6}; 3, 30.2×10^{-6}; 4, 51.5×10^{-6}; and 5, 103×10^{-6} M, in 98.8, 98.7, 98.6, 98.4 and 97.9% v/v ethanol, respectively. The graphs are adjusted to take the same potential (-300 mV) at 1×10^{-3} M sulphate. The concentrations of the three standard sulphate solutions are 1×10^{-5}, 1×10^{-4} and 1×10^{-3} M for graphs 1, 2 and 3; and 5×10^{-5}, 2×10^{-4} and 1×10^{-3} M for graphs 4 and 5

standard sulphate solution. Although the error can be changed when different points are taken for calibration, an over-simplified treatment of the theoretical calculation may also be the reason for systematic error.[6]

Interference Study

In this method, the ion which reacts with lead(II) or sulphate is regarded as the interferent. Chloride, hydrogen carbonate and phosphate react with lead(II) and calcium forms a precipitate with sulphate. Nitrate is also treated as one of the interferents.[1-3] The error in the determination of 1×10^{-4} M sulphate in the presence of the interferent(s) was examined under various reagent solution conditions.

Acidity of reagent solution

The acidity of the solution after the mixing of sample and reagent solutions can be an important factor, especially in relation to the conjugate anion of a weak acid such as carbonic or phosphoric acid. The acidity of the reagent solution was mainly changed using the carboxylic acid and its sodium salt. Table 2 gives the type and concentration of pH' adjuster together with the three determined parameters, E_0, S and K_{sp}. The slope values range from 28 to 35 mV decade^{-1}, the

solubility product K_{sp}, however, varied more than the slope. At a pH' value below 3.2 or above 6.5, the K_{sp} value is of the order of 1×10^{-11} M^2, which means that the precipitation reaction between sulphate and lead(II) is unfavourable outside of these pH' values.

Fig. 2 shows the effect of pH' in the continuous-flow determination of sulphate in the presence of interferents. Chloride showed a relative error of 10–28% that can be regarded as independent of pH'. The reproducibility of the relative error, when measured in the presence of chloride, was relatively poor; this is explained by the results of the dynamic response study as shown later.

Although both hydrogen carbonate and dihydrogen phosphate are the conjugate anions of weak acids, a marked difference was observed in their response to the acidity of the reagent solution. The behaviour of the phosphate seems to be as expected, i.e., the relative error increases with a decrease in the acidity, by promoting the dissociation of phosphoric acid to give ionic species such as $H_2PO_4^-$ and HPO_4^{2-}. Tanaka et al.[9] examined the response of a solid-state lead-selective electrode to phosphate and suggested that the monohydrogen phosphate dianion (HPO_4^{2-}) is the responsive ion. However, the titration curve of phosphoric acid with sodium hydroxide in 71% v/v ethanol gave two distinct inflection points at pH' 6.30 and 9.75. This means that the major ionic species of phosphate in the pH' range below 6.3 is $H_2PO_4^-$. Although the primary interfering species of phosphate is HPO_4^{2-}, dihydrogen phosphate might also affect the response of the lead-selective electrode.

A curious behaviour was observed for hydrogen carbonate. The relative error seemed to decrease to zero with a decrease in the acidity of the reagent solution. The titration curve of sodium carbonate with perchloric acid in 71% v/v ethanol gave two distinct inflection points at pH' 10.23 and 5.23. The pH' where the concentration ratio of H_2CO_3 to HCO_3^- is 1:1 appears to be ca. 8.0. (It should be noted that the first dissociation constant pK_{a1} of H_2CO_3 in water is 6.35.[10]) This result indicates that more than 99% of the carbonate might exist in the form of H_2CO_3 (or CO_2) in 71% v/v ethanol at a pH' below 6.0. An explanation of the origin of the interference from carbonate requires that further studies be carried out. Nitrate showed negligible interference in this pH' range.

A peculiar pattern was also observed from calcium, i.e., an increase in the relative error when the acidity decreased. Interestingly, the interference from calcium can be cancelled out to some extent (1–15%) in the presence of hydrogen

Table 1. Precision of five successive measurements of standard sulphate solutions of a sample of river water. Reagent: Pb(NO$_3$)$_2$ - 1 × 10^{-3} M CH$_2$ClCOOH - 1 × 10^{-2} M NaClO$_4$ in (i) 98.4 or (ii) 98.8% v/v ethanol. Concentrations of the three standard sulphate solutions were (i) 1 × 10^{-4}, 2 × 10^{-4} and 10 × 10^{-4} M and (ii) 1 × 10^{-5}, 10 × 10^{-5} and 100 × 10^{-5} M

[SO$_4^{2-}$]/ 10^{-5} M	Mean/ 10^{-5} M	SD/ 10^{-5} M	RSD, %	Error, %
(i)[Pb^{2+}] = 5.20 × 10^{-5} M—				
5.00	5.35	0.063	1.2	7.0
13.0	13.1	0.045	0.3	0.8
16.0	16.8	0.27	1.6	5.0
50.0	58.6	3.34	5.7	17
River water	12.8	0.0	0.0	—
(ii) [Pb^{2+}] = 1.00 × 10^{-5} M—				
2.00	1.77	0.071	4.0	−12
3.00	3.01	0.019	0.63	0.3
5.00	5.06	0.018	0.36	1.2
20.0	19.6	0.15	0.77	−2.0
50.0	49.6	0.39	0.79	−0.8

Table 2. Composition of reagent solutions of different acidity and the calibration parameters used with three standard sulphate solutions (1 × 10^{-5}, 1 × 10^{-4} and 1 × 10^{-3} M). Ionic strength adjuster: 1 × 10^{-2} M NaClO$_4$

Sample No.	pH'*	[Pb^{2+}]/ 10^{-6} M	Concentration of and type of pH' adjuster	Ethanol, % v/v	Conduc- tivity†/ μS cm^{-1}	E_0/ mV	S/mV decade^{-1}	K_{sp}/ 10^{-12} M^2
1	3.21	9.8	2.0 × 10^{-3} M HClO$_4$ ([NaClO$_4$] = 8 × 10^{-3} M)	98.7	346	−59.0	34.15	14.0
2	3.44	9.8	1.3 × 10^{-3} M CCl$_3$COOH	98.9	348	−59.3	33.46	9.10
3	3.91	10.1	2.0 × 10^{-3} M CH$_2$ClCOOH	98.7	317	−62.4	34.50	5.54
4	4.12	10.6	1.0 × 10^{-3} M CH$_2$ClCOOH	98.8	293	−20.1	33.92	3.44
5	4.58	10.4	1.0 × 10^{-3} M o-ClC$_6$H$_4$COOH	98.9	307	−59.3	33.79	2.75
6	4.80	9.9	1.0 × 10^{-3} M 3-ClC$_2$H$_4$COOH	98.9	281	−70.1	32.35	2.37
7	5.08	10.4	1.0 × 10^{-3} M CH$_3$COOH	98.5	297	−66.1	32.68	1.90
8	5.52	9.9	1.0 × 10^{-3} M CH$_3$COOH 1.0 × 10^{-4} M CH$_3$COONa	98.7	307	−75.3	33.04	3.10
9	5.88	9.6	1.0 × 10^{-3} M CH$_3$COOH 2.0 × 10^{-4} M CH$_3$COONa	98.6	292	−97.3	30.19	3.56
10	6.17	9.2	1.0 × 10^{-3} M CH$_3$COOH 5.0 × 10^{-4} M CH$_3$COONa	98.3	296	−113.9	28.89	7.12
11	6.46	10‡	1.0 × 10^{-3} M CH$_3$COOH 1.0 × 10^{-3} M CH$_3$COONa	98.7	315	−108.8	32.05	23.4

* Denoted value from the pH meter for the solution taken from the waste line.

† Measured for the solution taken from the waste line.

‡ Theoretical value is given because the titration of the reagent solution gave no clearly defined inflection point.

carbonate, by the formation of a calcium carbonate precipitate (the solubility product of $CaSO_4$ and $CaCO_3$ in water is 2.4×10^{-5} and $4.7 \times 10^{-9} M^2$, respectively[10]). In addition, the co-existence of chloride reduced the relative error to *ca.* zero in the pH' range 4–4.5.

Lead ion concentration

The effect of the concentration of lead(II) in the reagent solution on the relative error in the determination of 1×10^{-4} M sulphate in the presence of interferent(s) was examined. The composition of the reagent solution was 1×10^{-5}–10×10^{-5} M lead nitrate - 1×10^{-3} M monochloroacetic acid - 1×10^{-2} M sodium perchlorate in 98–99% ethanol.

The degree of interference, expressed as the relative error, decreased from −25 to −1% for calcium and from 26 to 9% for phosphate with an increase in the concentration of lead(II).

While the relative errors decreased from 29 to 4% for hydrogen carbonate and from 13 to 4% for chloride when increasing the lead ion concentration up to 5×10^{-5} M, they

then increased to 31 and 25%, respectively, at 1×10^{-4} M lead(II). The actual potential change caused by the co-existence of hydrogen carbonate was −4.9, −4.9, −4.9, −3.7 and −3.1 mV for *ca.* 1×10^{-5}, 2×10^{-5}, 3×10^{-5}, 5×10^{-5} and 10×10^{-5} M lead(II), respectively.

The relative error depends not only on the actual potential change caused by the co-existence of the interferent(s) but also on the sensitivity of the calibration graph at *ca.* 1×10^{-4} M sulphate. At 5×10^{-4} M lead(II), the relative error from all the interferents tested was less than 10%, which means that this concentration is the optimum for river water analysis taking into account the selectivity.

Ionic strength of reagent solution

The effect of the concentration of sodium perchlorate in the reagent solution on the relative error in the determination of 1×10^{-4} M sulphate in the presence of interferent(s) was examined. The composition of the reagent solution was 1×10^{-5} M lead nitrate - 1×10^{-3} M monochloroacetic acid - 2×10^{-3}, 5×10^{-3}, 10×10^{-3}, 20×10^{-3} or 50×10^{-3} M sodium perchlorate in 95–99% ethanol. The pH' of the reagent solution was approximately constant (4.0–4.1).

In a precipitation reaction, it is generally recognised that increasing the ionic strength is unfavourable to the formation of the precipitate owing to a decrease in the activity of the chemical species involved in the precipitation reaction. The increase of K_{sp} from 2×10^{-12} to 23×10^{-12} M^2 supports this statement. Hulanicki *et al.*[2] examined the potentiometric titration of sulphate with lead(II) perchlorate solution using a lead-selective electrode and recommended the addition of sodium perchlorate in order to eliminate the interference from calcium. Our results are consistent with their findings for calcium, as the degree of interference, expressed as the relative error, decreased from −40 to −6% on increasing the ionic strength of the reagent solution.

The interference from hydrogen carbonate also decreased proportionately from 49 to 13% with an increase in the logarithmic concentration of sodium perchlorate. However, for phosphate the relative error increased from 24 to 47% with an increase in the ionic strength, the reason for which is not obvious. The relative error from chloride varied from 3 to 13%, which is less significant in comparison with the effect of calcium, hydrogen carbonate or phosphate. No significant error was observed from nitrate (<4%).

Water content

The effect of water content in the reagent solution on the relative error in the determination of 1×10^{-4} M sulphate in the presence of interferent(s) was examined. The composition
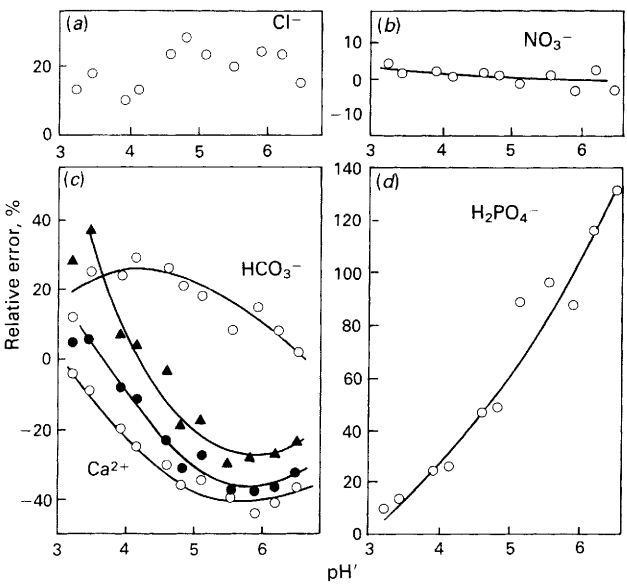

Fig. 2. Effect of acidity (pH') of reagent solutions on the relative error(%) of the continuous-flow determination of 1×10^{-4} M sulphate in the presence of interfering ions. Composition of the reagent solutions as given in Table 1. Concentration of interferents: Cl^-, 5×10^{-4} M; HCO_3^-, 1×10^{-3} M and Ca^{2+}, 5×10^{-4} M; NO_3^-, 5×10^{-4} M; and $H_2PO_4^-$, 1×10^{-5} M. ●, Results for SO_4^{2-} - HCO_3^- - Ca^{2+}; ▲, results for SO_4^{2-} - HCO_3^- - Ca^{2+} - Cl^-

Table 3. Effect of concentration of interferent on relative error in the determination of 1×10^{-4} M sulphate in the presence of interferent. Reagent: 1×10^{-5} M $Pb(NO_3)_2$ - 1×10^{-3} M $CH_2ClCOOH$ - 1×10^{-2} M $NaClO_4$ in 98.8% v/v ethanol. Error and standard deviation values for three replicate measurements of five samples

| Cl^-— | | | | HCO_3^-— | | | |
Concentration/10^{-4} M	Error, %	SD	RSD, %	Concentration/10^{-3} M	Error, %	SD	RSD, %
2	15.3	2.5	16	0.5	15.0	0.0	0
5	19.7	2.1	11	1	32.7	0.6	2
10	28.0	2.6	9	2	64.3	2.3	4
20	30.7	1.2	4	5	140	20	14
50	29.0	4.6	16	10	1390	47	3
Ca^{2+}—				$H_2PO_4^-$—			
Concentration/10^{-4} M	Error, %	SD	RSD, %	Concentration/10^{-5} M	Error, %	SD	RSD, %
2	−12.0	0	0	0.5	14.7	3.5	24
5	−27.0	0	0	1	23.3	3.1	13
10	−39.0	0	0	2	34.3	2.5	7
20	−51.7	0.6	1	5	52.7	4.0	8
50	−65.0	0	0	10	70.3	1.2	2

of the reagent solution was 1×10^{-5} M lead nitrate - 1×10^{-3} M monochloroacetic acid - 1×10^{-2} M sodium perchlorate in an ethanol - water mixture. The pH' of the solution after mixing decreased from 4.13 to 3.43 while the conductivity (as a measure of the ionic strength) increased from 293 to 505 µS cm^{-1} on increasing the water content from 1.2 to 60%. The determined parameters, S and K_{sp}, also changed with a change in the percentage volume of ethanol in the reagent solution, S

Fig. 3. Dynamic response of the lead(II)-selective electrode in the presence of interfering ions. Potential change caused by the addition of 0.1 ml of either: 1, 0.02 M Na$_2$SO$_4$; 2, 0.2 M NaHCO$_3$; 3, 0.1 M NaCl; or 4, 0.002 M KH$_2$PO$_4$ to a mixture of 50 ml of the reagent solution (1×10^{-5} M Pb(NO$_3$)$_2$ - 1×10^{-3} M CH$_2$ClCOOH - 1×10^{-2} M NaClO$_4$ in 98.8% v/v ethanol) and 20 ml of distilled water

Fig. 4. Dynamic response of the lead(II)-selective electrode in the presence of interfering ions. Potential change caused by the addition of: 1, 0.1 ml of 0.1 M Ca(NO$_3$)$_2$; 2, 0.002 M H$_2$PO$_4^-$; 3, 0.2 M NaHCO$_3$; or 4, 0.1 M NaCl to the solution, which was pre-equilibrated by the addition of 0.02 M Na$_2$SO$_4$ to a mixture of 50 ml of the reagent solution (composition as given in Fig. 3) and 20 ml of distilled water

decreasing from 33.92 to 13.10 mV decade^{-1} and K_{sp} increasing from 3.44 to 72.4 $\times$ 10^{12} M^2. The measured potentials at 75% did not give reasonable values for the three parameters, although the potential difference between 1×10^{-5} and 1×10^{-3} M standard sulphate solutions was about 17 mV.

With an increase in the water content, the precipitation reaction with lead(II) becomes unfavourable not only for sulphate but also for the other interferents. Consequently, the degree of interference, expressed as the relative error, decreased from 29 to 4% for hydrogen carbonate and from -25 to -8% for calcium while the relative error increased from 13 to 41% for chloride on increasing the water content from 1.2 to 50%. The relative error varied in the range 56–15% for phosphate. No suitable conditions which eliminated the interference from all the ions tested was found in this experiment.

Interferent concentration

Table 3 gives the relative error in the determination of 1×10^{-4} M sulphate in the presence of each interferent at five different concentrations. Although the concentration range is different for each, the relative error increased with an increase in the concentration of interferent. However, chloride did not show the proportionality shown with the other interferents, at least in the concentration range 10×10^{-4}–50×10^{-4} M. This result seems to be related to the dynamic response behaviour of the lead-selective electrode in the presence of chloride as discussed later.

The relative error in the presence of hydrogen carbonate increased noticeably in the concentration range 1×10^{-3}–1×10^{-2} M. Preferential precipitation of lead carbonate seems to occur over the formation of lead sulphate, when the concentration ratio of hydrogen carbonate to sulphate becomes 100:1 (the solubility product of PbCO$_3$ and PbSO$_4$ in water is 1.5×10^{-13} and 1.7×10^{-8} M^2, respectively[10]).

The reproducibility of the relative error in the presence of calcium was excellent at every concentration. These results seem to suggest that the calcium ion may not interact with the surface components of the PbS - Ag$_2$S based lead-selective electrode and the reaction between calcium and sulphate occurs only in the solution phase. The interference from the co-existence of nitrate was insignificant ($<5\%$) at concentrations 50-fold greater than that of 1×10^{-4} M sulphate.

Dynamic response of lead-selective electrode

Fig. 3 shows the potential - time response curve obtained upon the addition of the sodium or potassium salt of the anions to the pre-equilibrated lead(II) solution. The potential showed a rapid change in the negative direction on the addition of sulphate owing to the formation of a lead sulphate precipitate. However, the final total potential change compared with the
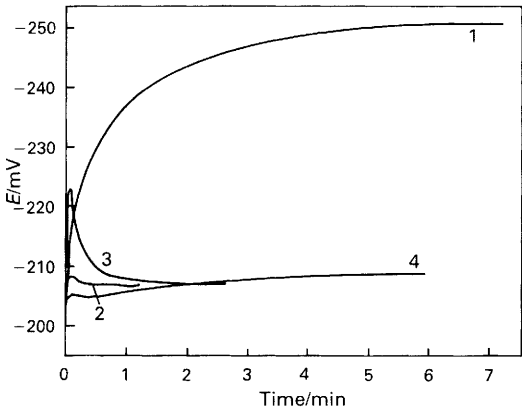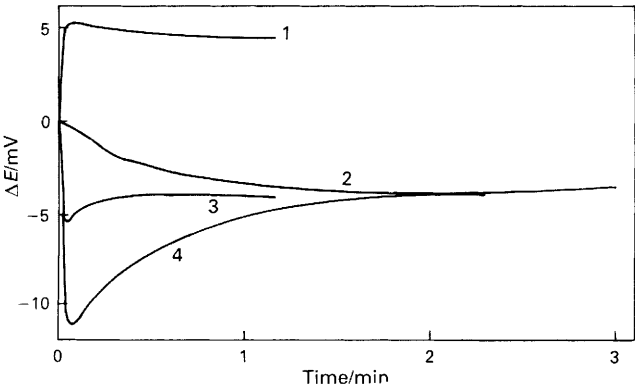
Table 4. Results of natural water analysis by continuous flow and turbidimetry. Reagent: 5.20×10^{-5} M Pb(NO$_3$)$_2$ - 1×10^{-3} M CH$_2$ClCOOH - 1×10^{-2} M NaClO$_4$ in 98.4% v/v ethanol. Determination of interferent concentration was carried out using the following methods: argentimetric titration with silver nitrate for chloride; complexometric titration with EDTA for calcium; spectrophotometry with ammonium molybdate for phosphate. Alkalinity at pH 4.8 was measured and taken as an index of hydrogen carbonate concentration. Filtered samples were used in common for both the flow system and the turbidimetric determination

| | [SO$_4^{2-}$]/10^{-4} M | | Concentration of possible interferent | | | |
Sample	Flow system	Turbidi-metry	[Cl$^-$]/10^{-4} M	[Ca^{2+}]/10^{-4} M	[PO$_4$]/10^{-5} M	Alkalinity/10^{-4} equiv. l^{-1}
Lake Biwa water ..	1.19	1.30	2.91	2.68	<0.1	6.26
Pond water	0.787	0.874	0.84	1.26	<0.1	2.50
River water 1 ..	0.987	1.03	2.21	1.88	0.24	3.55
River water 2 ..	1.19	1.09	1.58	1.94	<0.5	4.02
River water 3 ..	1.19	1.24	2.47	2.70	<0.1	6.43
River water 4 ..	1.82	1.87	3.96	3.16	0.95	7.66
River water 5 ..	2.13	2.20	4.26	3.54	0.97	8.55
Tap water	1.58	—	2.85	2.68	—	4.37

initial values for the other three interferents was relatively small. Except for phosphate, which had a final concentration 10-fold lower than sulphate, the potential - time curves for chloride and hydrogen carbonate indicate that the formation of lead chloride or lead carbonate precipitates does not occur as readily as that of lead sulphate. Moreover, the large non-monotonic transient signal as shown in the first part of the potential - time curve of chloride, is similar to that following the activity step of the interfering ion in the so-called two-ion range.[8]

Fig. 4 shows the potential - time curves caused by the addition of the interferents to the lead(II) solution that had been pre-equilibrated by the addition of sulphate. The negative transient potential excursion also appeared on the addition of chloride. The adsorption of chloride on the surface of the PbS - Ag_2S based lead-selective electrode may play an important role in the occurrence of this type of transient signal, as was previously reported to be the situation in the non-monotonic dynamic response curve obtained with an AgI based iodide-selective electrode in the presence of a large excess of bromide.[8] In this study, a certain potential in the relaxation part of the potential - time curve was regarded as an equilibrium potential in the presence of chloride. This is one of the reasons for the poor reproducibility and the anomalous concentration dependence of interference from chloride.

Water Analysis

Analysis of discrete samples

Table 4 gives the results of the natural water analysis. The concentrations of the possible interferents are also listed in the table. The results obtained with the flow system are consistent with those of the turbidimetric determination, which means that the interference is not significant. Although the filtered samples were used for the purpose of comparison with the

turbidimetric method, any pre-treatment, including filtration, is not necessary with the flow system. This is the merit of this system in practical analysis. The time required for the analysis of these samples was about 2 h including calibration.

Continuous determination of sulphate

Long-term stability of the continuous-flow system was examined using two different lead(II) concentrations in a reagent solution containing 1×10^{-3} M monochloroacetic acid and 1×10^{-2} M sodium perchlorate, i.e. 1×10^{-5} M for rain water analysis and 5×10^{-5} M for river water analysis. With the former, the fluctuation of potential in the measurement of 1×10^{-5} M standard sulphate solution was ± 0.6 mV h^{-1}. In the latter instance, the potential change during 1 h in the measurement of Tara river water was 5.7 mV, which corresponded to an error of -8% compared with the initial concentration (1.68×10^{-4} M).

Rain water. Fig. 5 shows the continuous analysis of rain water falling on September 19, 1989, at Shiga University (Otsu, Japan). It began to rain at about 13:00 became very heavy from 13:50, stopping once at 16:17 and re-starting 5 min later and then finishing finally at 17:01. The concentration of sulphate fell below 1×10^{-6} M during a certain period when it was raining heavily, whereas it gradually increased as the rainfall came to an end at 16:17 and 17:01. Although the sensitivity of the system was insufficient for the determination of the concentration of sulphate below 1×10^{-6} M, the system is useful for the continuous monitoring of falling rain water.

River water. The continuous analysis of Tara river water in Otsu city, which is polluted by domestic sewage from the Ishiyama housing estates, was carried out on October 12 and 20, 1989. Fig. 6 shows the result of the second observation. The concentration of sulphate was almost constant during the periods of observation and nearly the same on both occasions (1.4×10^{-4}–1.5×10^{-4} M). As sulphate is one of the major components in natural waters, its concentration seems to be less affected by the artificial pollution than the other components, such as the nitrogen from ammonium.

The effects of various factors which can affect the relative error in the continuous-flow determination of sulphate have been examined. The main factor, which has not been examined yet, is the type of solvent used. Further study may be necessary on the response mechanism of a lead-selective electrode in the presence of interferent(s).

Fig. 5. Continuous analysis of rain water on September 19, 1989 at Shiga University (Otsu, Japan). Reagents: 10.6×10^{-6} M Pb(NO$_3$)$_2$ - 1 $\times$ 10^{-3} M CH$_2$ClCOOH - 1×10^{-2} M NaClO$_4$ in 98.8% v/v ethanol. Sampling rate, 1.0 ml min^{-1}. A standard solution of 1×10^{-5} M Na$_2$SO$_4$ was measured during the period indicated by "St.". Corrected values based on the results of calibration between 1×10^{-5} and 1×10^{-6} M have been plotted below 1×10^{-5} M and the data below 1×10^{-6} M have been omitted from the figure

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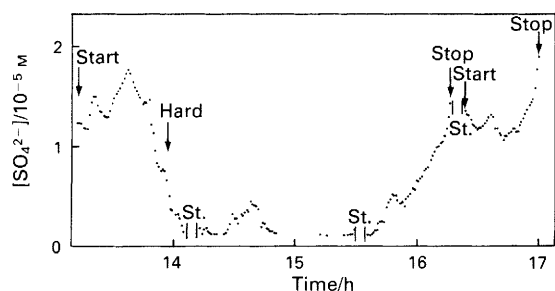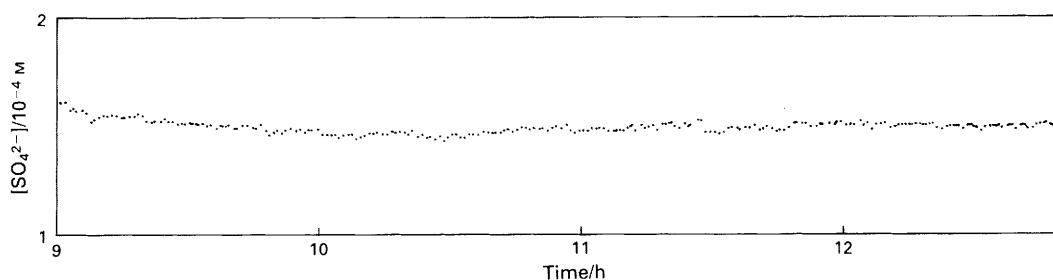**Fig. 6.** Continuous analysis of river water (Tara river, Otsu, Japan) on October 20, 1989. Reagents: 51.0×10^{-6} M Pb(NO$_3$)$_2$ - 1 $\times$ 10^{-3} M CH$_2$ClCOOH - 1×10^{-2} M NaClO$_4$ in 98.4% v/v ethanol. Sampling rate, 1.0 ml min^{-1}

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