HIRANUMA APPLICATION DATA	Automatic Titrator	Data No.	C6	Apr. 5, 2019
Detergents・Bath additives・Cosmetics	**Quantitative determination of sodium sulfate in bath additive**			

1. Abstract

The precipitation titration using lead ion-selective electrode achieves the measurement of sulfate ions. Lead sulfate is generated by adding lead nitrate to sulfate ion. The potential reading with lead ion-selective electrode differs depending on the concentration of sulfate ion in sample solution. The maximum change in potential is observed when it reaches the equivalent point of sulfate and lead ions. The concentration of sulfate ion is determined by the titrant volume consumed until it reaches the inflection point.

$$SO_4^{2-} + Pb(NO_3)_2 \rightarrow PbSO_4 + 2NO_3^-$$

This report introduces an example of the measurement for sulfate ion in bath additive with using lead ion-selective electrode.

2. Configuration of instruments and reagents

(1) Configuration

Main unit	:	Hiranuma Automatic Titrator COM series	
Electrodes	:	Lead ion-selective electrode	Pbi-081
		Glass-reference combination electrode	GE-501BZ

(2) Reagents

Titrant	:	0.01 mol/L lead nitrate standard solution Dissolve 1.6560 g of lead (II) nitrate in DI water and prepare 500 mL solution.
Standardization solution	:	0.01 mol/L sulfuric acid standard solution
Solvent	:	50 mL of diluted methanol Mix methanol and DI water with 4:1 volume ratio.
Additive solution	:	Diluted nitric acid (10 % [v/v])

3. Measurement procedure

(1) Standardization of 0.01 mol/L lead nitrate standard solution.

i) Dispense 10 mL of 0.01 mol/L sulfuric acid standard solution into a 100 mL beaker with volumetric pipette.

ii) Add 50 mL of solvent and stirring bar to the beaker.

iii) Immerse the electrodes into sample solution and titrate with 0.01 mol/L lead nitrate standard solution.

(2) Measurement of sodium sulfate in bath additive

i) Accurately weigh about 0.4 g of bath additive with 0.1 mg digit. Dissolve it with DI water and prepare 200 mL solution using volumetric flask.

ii) Dispense 5 mL of the above solution into a 100 mL beaker with a volumetric pipette.
This aliquot of sample solution contains about 0.01 g of sample (0.4 g × 5 mL/200 mL).

iii) Add 50 mL of solvent and a stirring bar to the beaker.

vi) Immerse the electrodes into sample solution and add a few drops of diluted nitric acid by a dropper with reading the pH using GR-501B to adjust the pH to about 4. Start titration with 0.01 mol/L lead nitrate standard solution.

4. Measurement conditions and results

Examples of titration conditions

(1) Standardization of 0.01 mol/L lead nitrate standard solution.

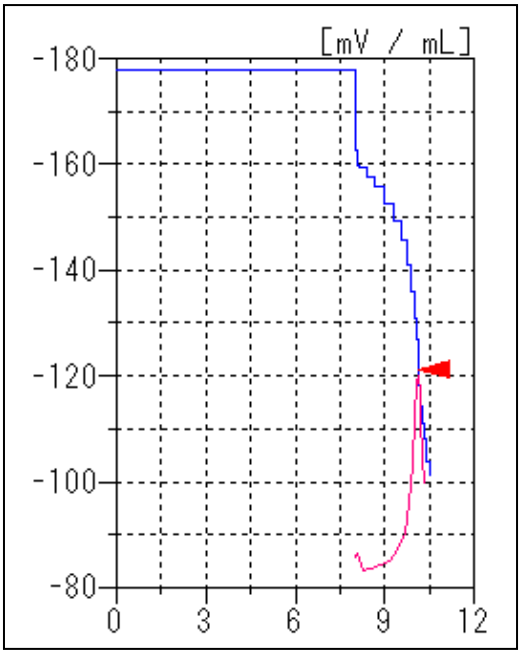
Cnd. No.	1							
Method	Auto		Constant No.	1		Mode No.	8	
Buret No.	1		Size	10	mL	Pre Int	0	sec
Amp No.	2		Blank	0	mL	Del K	5	
D.Unit	mV		Morality	0.01	mol/L	Del Sens	0	mV
S- Timer	0	sec	Factor	0.997		Int Time	5	sec
C.P. mL	8	mL	K	0		Int Sens	3	mV
T.Timer	10	sec	L	0		Brt Speed	2	
D.P. mL	0	mL	Unit	Fact1		Pulse	40	
End Sens	50		Formula					
Over mL	0.3	mL		S/(D-B)*F				
Max Vol.	20	mL	Decimal Places	3				
			Auto input parameter		None			

(2) Titration of sodium sulfate with lead nitrate

Cnd. No.	1							
Method	Auto		Constant No.	1		Mode No.	8	
Buret No.	1		Size	0.01	g	Pre Int	0	sec
Amp No.	2		Blank	0	mL	Del K	5	
D.Unit	mV		Morality	0.01	mol/L	Del Sens	0	mV
S- Timer	0	sec	Factor	0.9849		Int Time	5	sec
C.P. mL	0	mL	K	142.04		Int Sens	3	mV
T.Timer	0	sec	L	0		Brt Speed	2	
D.P. mL	0	mL	Unit	%		Pulse	40	
End Sens	50		Formula					
Over mL	0.3	mL		(D-B)*K*F*M/(S*10)				
Max Vol.	20	mL	Decimal Places	3				
			Auto input parameter		None			

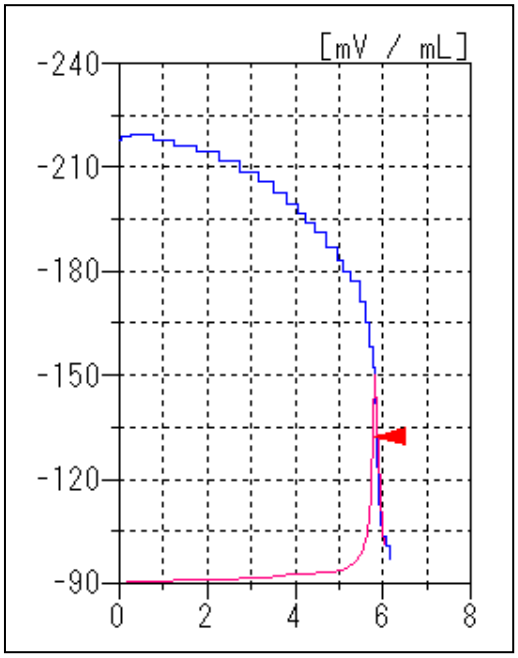
Measurement results

(1) Standardization of 0.01 mol/L lead nitrate standard solution



Number of Measurement	Size (mL)	Titrant Volume (mL)	Factor
1	10	10.118	0.9854
2		10.129	0.9843
		Average	0.9849

(2) Titration of sodium sulfate with lead nitrate



Number of Measurement	Actual Sample Size (g)	Titrant Volume (mL)	Concentration (%)
1	0.0100	5.826	81.503
2		5.832	81.587
3		5.867	82.077
4		5.841	81.713
5		5.834	81.615
Statistic calculation		Average	81.70 %
		Standard deviation	0.22 %
		Coefficient of variation	0.27 %

Example of titration curves

*Some measurement would not be possible depending on optional configuration of system.

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5. Note

(1) The reading of the potential might decrease with repeated use of the lead ion-selective electrode. Polishing the surface of the lead ion-selective electrode with a fine sandpaper (P800 or finer) improves the condition of the electrode.

(2) The response sensitivity of the lead ion-selective electrode might decrease because of the influence of coexisting materials and the measurement would be failed. There is a possibility that this method cannot be applied for a sample containing multiple components like plating solution.

(3) The total amount of sodium sulfate and magnesium sulfate are detected when the sample contains both substances. The magnesium ion of magnesium sulfate can be determined by photometric titration. The concentration of sodium sulfate can be calculated by subtracting the concentration of magnesium sulfate from the result of total amount.

Keywords：Sulfate ion, Precipitation titration, Lead ion-selective electrode, Bath additive

*Some measurement would not be possible depending on optional configuration of system.