Application Note

Determination of inorganic sulfate in bioethanol

Industry	Chemicals
Instrument	Automatic potentiometric titrator
Measurement method	Precipitation titration
Standards	ASTM D7318

1. Scope

Bioethanol for fuel is sometimes contaminated with inorganic sulfates, which can cause engine deterioration and air pollution. Therefore, it is necessary to confirm that the inorganic sulfate is less than a specified amount. This Application Note introduces an example of measuring sulfate ion concentration in ethanol using the method specified by ASTM D7318.
The quantification method for this standard is shown below.
In a solution of 100 g of sulfate-free ethanol, add 0.20 mL of 0.01 mol/L aqueous sulfate standard solution, and use the titration volume of this solution as a blank test value. Add the same volume of the aqueous sulfate standard to 100 g of ethanol sample. The difference in titration volume from the blank test is defined as the concentration of sulfate in the sample.

2. Precautions

1) Before starting measurements each day, purge the titrant several times between the reagent bottle and the burette to equalize the titrant concentration, then discharge about 10 mL of the titrant between the burette and the titration nozzle.
2) This measurement uses the reagents harmful to the human body. When you follow this application note, wear masks, gloves, protective equipment, etc.

3. Apparatus

Main unit	Automatic potentiometric titrator (Preamplifier STD)
Electrode	Lead ion electrode, Double junction reference electrode
	Outer cylinder inner liquid 1 mol/L lithium chloride solution (ethanol solvent)

4. Reagents

Titrant	0.025 mol/L Lead nitrate standard solution
Additive reagents	0.01 mol/L Aqueous sulfate standard
	0.1 mol/L Perchloric acid solution
	Ethanol* (for blank test) *Used a sulfate-free reagent

5. Procedure

-Blank test-

1) Collect 100 g of ethanol (sulfate-free) and measure the mass.
2) Add 0.20 mL of 0.01 mol/L aqueous sulfate standard.
3) Add 1 mL of 0.1 mol/L perchloric acid solution. Check the pH with pH test paper (range of 3 to 5). If the sample exceeds pH 5, add 0.1 mol/L perchloric acid solution as necessary, and adjust to a pH of 3 to 5.
4) Titrate with 0.0025 mol/L lead nitrate standard solution.

-Measurement-

1) Collect 100 g of ethanol sample and measure the mass.
2) Add 0.20 mL of 0.01 mol/L aqueous sulfate standard.
3) Add 1 mL of 0.1 mol/L perchloric acid solution. Check the pH with pH test paper (range of 3 to 5). If the sample exceeds pH 5, add 0.1 mol/L perchloric acid solution as necessary, and adjust to a pH of 3 to 5.
4) Titrate with 0.0025 mol/L lead nitrate standard solution.

6. Calculation

Sulfate ion concentration (mg/kg) = (EP1-BL1) × TF × C1 × K1/S

EP1	Titration amount (mL)
BL1	Titration amount (mL) of blank test = 0.7955 (mL)
TF	Factor of titrant = 1.0259
C1	Concentration conversion coefficient = 0.24014
K1	Unit conversion factor = 1000
S	Sample size (g)

7. Example

— Parameter —

<Titration Mode> Auto Intermit

<Titration Form> EP Stop

<Titration Parameter>

Channel, Unit(For Control)	Ch1, mV
Channel, Unit(For Reference)	Off
pH Polarity	Standard
Type of Titration	Not Check.
EP Direction	Auto
Wait Time	30 (s)
Dose Mode	Off

<Control Parameter>

Number of EP	1
End Sense	Set
Gain	3
Data Sampling	Standard
Control Speed Mode	Standard
Other Control	Standard
Auto Int. Mode	Standard (Sample)
	Blank (Blank)
Stirrer Speed	4

（The above condition is an example. The setting condition depends on the model.）

— Measurement results —

The measurement results for each sample are shown in Tables 1 and 2.

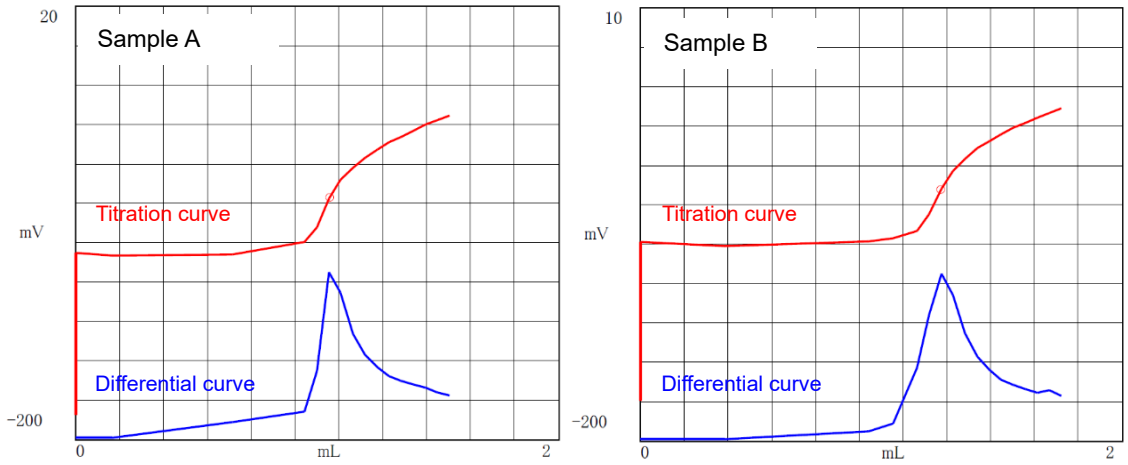
Table 1 Sample A

	Sample (g)	Titration (mL)	Conc. (mg/kg)
1	100.0141	1.0527	0.63
2	100.0755	1.0303	0.58
3	100.0451	1.0490	0.62
Average	-	-	0.61
SD	-	-	0.03
RSD (%)	-	-	4.3

Table 2 Sample B

	Sample (g)	Titration (mL)	Conc. (mg/kg)
1	100.0603	1.2495	1.12
2	100.0008	1.2220	1.05
3	100.0255	1.2469	1.11
Average	-	-	1.09
SD	-	-	0.04
RSD (%)	-	-	3.5

— Example of titration curve —



Example of titration curve

8. Reference

ASTM D7318-19 Standard Test Method for Existent Inorganic Sulfate in Ethanol by Potentiometric Titration