Metrohm

Thermo. Titr. Application Note No. H-109

Title:	**Determination of Components of Mixtures of Sulfuric Acid, Hydrofluoric Acid, and Ammonium Bifluoride**

***Scope*:**	Determination of mixtures of sulfuric acid, hydrofluoric acid, and ammonium bifluoride

***Principle*:**	Results from three separate single endpoint titrations are used to calculate the mean. The mixture of H_2SO_4, HF and $NH_4F.HF$ contains H^+ from H_2SO_4, HF and $NH_4F \cdot HF$, SO_4^{2-} from H_2SO_4, and F^- from HF and $NH_4F \cdot HF$. Analysis of total H^+ („total acids“) by NaOH titration, F^- by titrating with $Al(NO_3)_3$ („total fluoride“) and SO_4^{2-} by titrating with $BaCl_2$ provides the information required to determine the composition of the mixture.

Reagents:	*Sodium hydroxide solution, c(NaOH) = 2 mol/L*, prepared from A.R. NaOH and deionized water, standardized against potassium hydrogen phthalate. *Barium chloride solution, c($BaCl_2$) = 1 mol/L*, standardized against anhydrous sodium sulfate. *Aluminum nitrate solution, c($Al(NO_3)_3$) = 0.5 mol/L*, standardized against anhydrous sodium fluoride. *Mixed buffer solution.* Potassium acetate (anhydrous), 134.9 g/L; sodium acetate (anhydrous), 54.7 g/L; glacial acetic acid, 115 g/L. *Synthetic acid mixture.* A synthetic acid mixture was prepared from A.R. H_2SO_4 (~97% w/w) , A.R. HF solution (~48% w/w) and L.R. $NH_4F \cdot HF$.

Method:

1. "Total Fluoride" titration:
Weigh accurately approximately 1 g of acid mixture into a clean, dry 75 mL PP titration beaker. The sample is placed without further dilution in the rack of the sample processor. The automated titration program dispenses 30 mL of mixed acetate buffer into the beaker before starting titrant addition. The titration with 0.5 mol/L $Al(NO_3)_3$ is pursued to a single exothermic endpoint. The result is stored as % HF in "Configuration" as a Common Variable (CV) for later computation.

Basic experimental parameters:

Titrant dose rate:	4 mL/min
Filter factor:	50
Endpoint criterion:	-50
Stop volume:	5 mL

2. Titration of sulfuric acid component:
Weigh accurately approximately 1 g of acid mixture into a clean, dry 75 mL PP titration beaker. After adding 30 mL DI water, place the sample in the rack of the sample processor. The titration with 1 mol/L $BaCl_2$ is pursued to a single exothermic endpoint. The result is stored as % H_2SO_4 in "Configuration" as a CV for later computation.

Basic experimental parameters:

Titrant dose rate:	4 mL/min
Filter factor:	50
Endpoint criterion:	-12
Stop volume:	5 mL

3. *Titration of total acids*
Weigh accurately approximately 1 g of acid mixture into a clean, dry 75 mL PP titration beaker. After adding 30 mL DI water, the sample is placed in the rack of the sample processor. The titration with 2 mol/L NaOH is pursued to a single exothermic endpoint. The result is stored as % H_2SO_4 in "Configuration" as a CV for later computation.

Basic experimental parameters:

Titrant dose rate:	4 mL/min
Filter factor:	50
Endpoint criterion:	-100
Stop volume:	10 mL

Note on performance of the titration sequence.
The sequence of titrations to be performed by the analyst should be as follows:
- Total fluoride (titration with $Al(NO_3)_3$
- Sulfuric acid (titration with $BaCl_2$)

- Total acids (titration with NaOH)

Note that while the “total fluoride” and “sulfuric acid” titrations may be alternated, the “total acids titration must be performed last, as this method contains the final calculations.

Determination of titration systematic endpoint errors (as “blanks”)

It is necessary to determine blank values for each of the three titrations. In each case, different masses of acid mixture were weighed into a set of titration beaker with more or less equal increments (from ~0.25 to 1 g). The beakers were prepared and titrated according to the methods outlined above. Between 5 and 7 aliquots were employed for determination of the blanks.

The contents of each vessel were titrated successively using a specially-constructed automated titration program; which also conducted a regression analysis on the results. This reported a systematic error (“blank”) for each endpoint as the y-intercept in mL; as well as the correlation coefficient for each determination. The respective blank values in mL are subtracted from the titrant volume for each endpoint. Blank values for each determination are stored in “Configuration” as CVs for computation of results.

Setting up for analysis:

Loading methods. Example methods are supplied with this AN. Import these methods using Method Manager. Note that these methods have been prepared for use with an 814 Sample, so adjustments will need to be made to the methods if other equipment configurations are used.

Preparing CVs. Prepare CVs for the following values:

CV no.	*CV name*	*Calc. Code*
CV1	Total fluoride blank	A
CV2	Sulfuric acid blank	B
CV3	Total acids blank	C
CV4	% Total fluoride	D
CV5	% Sulfuric acid	E

Calculation Methodology:

The basis of the calculation methodology is that all items are reduced to an HF equivalent, prior to re-calculating to a final formula.

Total fluoride titration

$$\% \text{ HF} = \frac{(\text{EP mL} - \text{A mL}) \times c(Al(NO_3)_3) \times M(HF) \times 6 \times 0.1}{\text{Sample mass, g}}$$

(saved as CV4 = D)

Sulfuric acid titration

$$\% \text{ } H_2SO_4 = \frac{(\text{EP mL} - \text{B mL}) \times c(BaCl_2) \times M(H_2SO_4) \times 0.1}{\text{Sample mass, g}}$$

(saved as CV5 = E)

Total acids titration expressed as % HF

$$\% \text{ TA as HF} = \frac{(\text{EP mL} - \text{C mL}) \times c(NaOH) \times M(HF) \times 0.1}{\text{Sample mass, g}}$$

(call this “F”)

Express % H_2SO_4 as % HF

$$\% \text{ HF} = \frac{E \times 2 \times M(HF)}{M(H_2SO_4)}$$

(call this “G”)

Calculate HF from free HF and HF component of $HH_4F \cdot HF$

%HF from HF and $HH_4F \cdot HF$ = F – G

(call this “H”)

Calculate NH_4F component of $NH_4F \cdot HF$ as % HF

%NH_4F as %HF = D – H

(call this “I”)

Calculate % free HF in mixture

% HF = H – I

Calculate $NH_4F \cdot HF$ in mixture

$$\% \text{ } NH_4F \cdot HF = \frac{I \times M(NH_4F \cdot HF)}{2 \times M(HF)}$$

Results:

Analysis of synthetic acid mixture:

% H_2SO_4:	40.3 ± 0.2% (n = 6)
% HF:	7.5 ± 0.1% (n = 6)
% $NH_4F \cdot HF$:	12.8 ± 0.2% (n = 6)

Titration Plots:

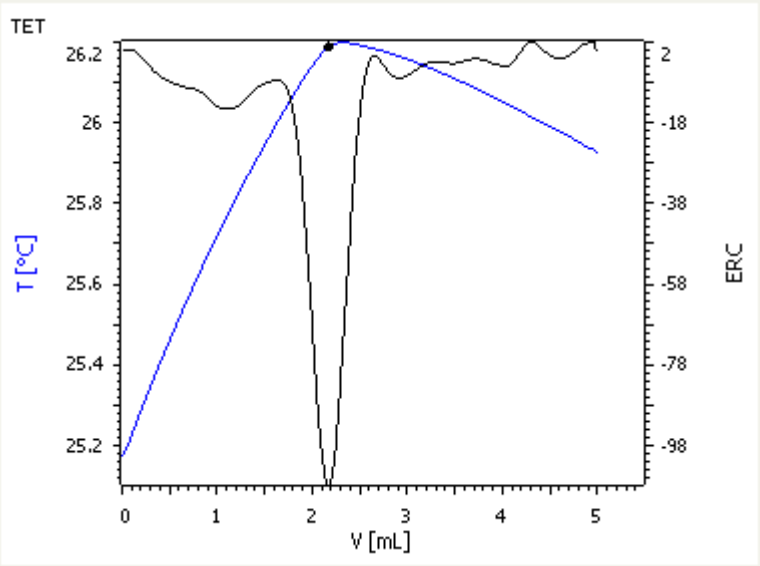

Fig. 1. Thermometric titration of total fluoride concentration with $c(Al(NO_3)_3) = 0.5$ mol/L

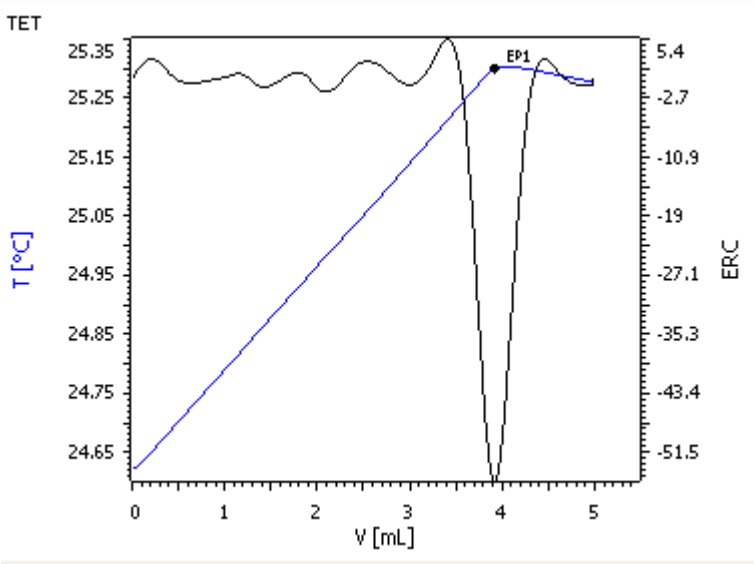

Fig. 2. Titration of sulfuric acid component with $c(BaCl_2) = 1$ mol/L

Titration Plots (continued):

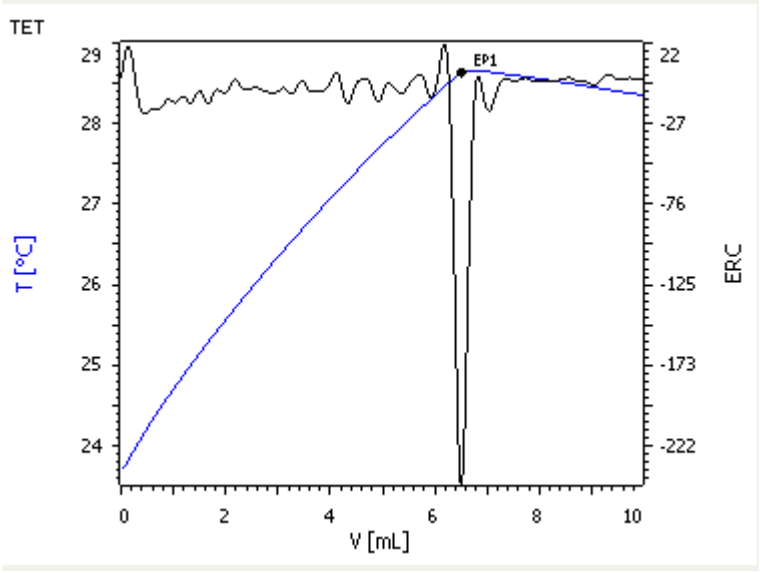

Fig. 3. Titration of total acids in mixture with c(NaOH) = 2 mol/L