Metrohm

Thermo. Titr. Application Note No. H-092

Title:	Analysis of zirconium acetate

Scope:	Automated determination of the zirconium content of zirconium acetate, as well as other zirconium compounds which can be rendered soluble as zirconium acetate.

Principle:	An aliquot of zirconium acetate is diluted with an ionic adjustor solution. A known excess of standardized KF solution is then added, followed by an acetate buffer containing sodium and potassium ions. Under these conditions, fluoride reacts with zirconium exothermically to precipitate, probably as a complex zirconium octafluoride.

| *Reagents*:	*Titrant 1:* 2mol/L KF
	Titrant 2: 1mol/L $Al(NO_3)_3$
	Acetate buffer (pH4.5): Dissolve 130.9 g anhydrous potassium acetate and 54.7 g anhydrous sodium acetate in 60mL DI water, and add 115mL glacial acetic acid. Make to 1000mL with DI water
	Ionic adjustor: Mixed 1 mol/L potassium chloride, 1mol/L sodium chloride solution
	Zirconium acetate ("Zr(OAc)₄"): Aldrich cat. no. 413801; zirconium acetate, solution in dilute acetic acid, approximately 15-16% w/w

Method:	**Basic Experimental Parameters:**	
	KF pre-dose (mL):	12.5
	KF pre-dose rate (mL/min)	40
	Delay before buffer pre-dose (secs.)	120
	Buffer pre-dose (mL)	10
	Buffer delivery rate (mL/min.)	40
	$Al(NO_3)_3$ delivery rate (mL/min)	5
	No. of exothermic endpoints	1
	Data smoothing factor	72
	Maximum dose (mL)	5
	Stirring speed (802 stirrer)	8
	Delay before start (secs.)	20

Sample Preparation

Weigh ~1mL (~1.3g) $Zr(OAc)_4$ solution or an equivalent amount of Zr (~2.25 mmol) into a titration beaker. Add 10mL ionic adjustor solution and 20mL DI water.

Titration

The titration starts with a pre-dose of KF solution, followed by the addition of 10mL of acetate buffer 120 secs. after the start. Addition of titrant then commences after a further 20 seconds delay. The titration stops automatically after the single exothermic endpoint is reached.

Example:	*Aldrich cat. no. 413801; zirconium acetate, solution in dilute acetic acid, approximately 15-16% w/w, n = 11 replicate titrations.*
	Zr% w/w = 16.00±0.05%

Calculations:

$$\% \ Zr \ w/w = \frac{((V_1 - (\frac{V_2 \times 6 \times m_2}{m_1})) \times 91.224 \times m_1 \times 100)}{(S \times 8 \times 1000)}$$

Legend:

Atomic mass Zr	91.224	Sample mass, g	S
Molarity KF, mol/L	m_1	KF pre-dose, mL	V_1
Molarity $Al(NO_3)_3$, mol/L	m_2	Endpoint vol., back-titration, mL	V_2

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Thermometric Titration Plot:

Legend:
Red = solution temperature curve
Black =second derivative curve (for endpoints)

Zr by KF and Al back-titration - C:\Program Files\Titrotherm\MDF\Zr acetate-22.MDF

EP1: 1.657ml
IP1,D2 Min -I
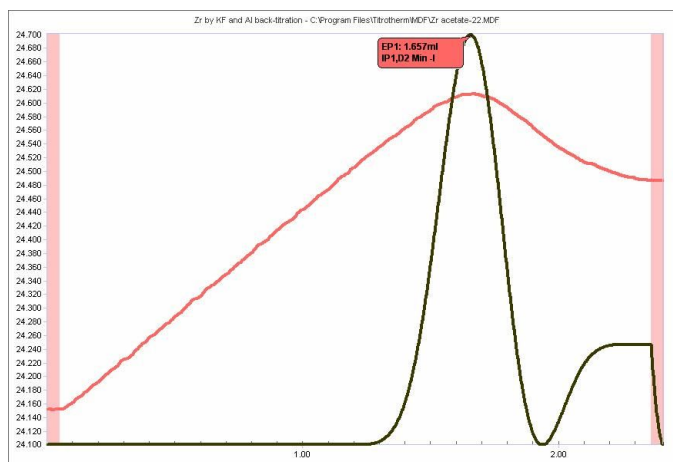
Back-titration of excess KF in presence of KOAc/NaOAc/HOAc buffer solution