Metrohm

Application Bulletin 223/2 e

Fully automated determination of uranium

Branch

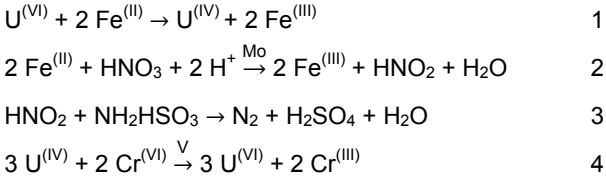
Energy, power plant

Keywords

Titration; uranium; Davies and Gray; automation; branch 16

Summary

This Bulletin describes the automated determination of uranium according to the Davies and Gray method: Uranium(VI) is reduced with iron(II) to uranium(IV) in a highly concentrated phosphoric acid medium (1). The excess of iron(II) is then oxidized to iron(III) with nitric acid in the presence of a molybdenum catalyst (2). The nitrous acid formed in this reaction is destroyed by sulfamic acid (3) and finally the uranium(IV) is titrated with potassium dichromate in the presence of a vanadium catalyst (4).



$$U^{(VI)} + 2\ Fe^{(II)} \rightarrow U^{(IV)} + 2\ Fe^{(III)} \quad (1)$$

$$2\ Fe^{(II)} + HNO_3 + 2\ H^+ \xrightarrow{Mo} 2\ Fe^{(III)} + HNO_2 + H_2O \quad (2)$$

$$HNO_2 + NH_2HSO_3 \rightarrow N_2 + H_2SO_4 + H_2O \quad (3)$$

$$3\ U^{(IV)} + 2\ Cr^{(VI)} \xrightarrow{V} 3\ U^{(VI)} + 2\ Cr^{(III)} \quad (4)$$

Instruments

- Sample changer
- Titrator with DET mode

Electrodes

Combined Pt-ring electrode	6.0451.100

Reagents

- Type 1 water (ASTM) (ultrapure water)
- Iron(II)sulfate heptahydrate, $FeSO_4 \cdot 7H_2O$, analytical reagent grade
- Sulfuric acid, $w(H_2SO_4) = 98\%$, $\Phi(H_2SO_4) = 50\%$ (v/v), $c(H_2SO_4) = 1$ mol/L, $c(H_2SO_4) = 0.1$ mol/L
- Sulfamic acid, NH_2HSO_3, laboratory reagent grade
- Potassium dichromate, $K_2Cr_2O_7$, analytical reagent grade
- Ortho-phosphoric acid, $w(H_3PO_4) = 85\%$, analytical reagent grade
- Ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$
- Nitric acid, $w(HNO_3) = 65\%$, $c(HNO_3) = 10$ mol/L
- Vanadyl sulfate monohydrate, $VOSO_4 \cdot H_2O$, analytical reagent grade
- Ammonium fluoride, NH_4F, analytical reagent grade

Solutions

Iron(II)sulfate solution $\beta(FeSO_4 \cdot 7H_2O) = 280$ g/L	100 mL $w(H_2SO_4) = 98\%$ is added to 600 mL ultrapure water. Then 280 g ± 0.1 g of $FeSO_4 \cdot 7H_2O$ is added to the diluted sulfuric acid. After dissolving the $FeSO_4$, the solution is left to cool down to room temperature and is made up to 1000 mL. This solution may be used for 7 days.
Sulfamic acid solution $\beta(NH_2HSO_3) = 150$ g/L	150 ± 0.1 g sulfamic acid is dissolved in 700 mL ultrapure water (this may require gentle heating). After the solution is cooled down to room temperature it is diluted to 1 L. This solution may be used for up to one month.
Titrant $\beta(K_2Cr_2O_7) = 12.5$ g/L	25 ± 0.1 g $K_2Cr_2O_7$ is weighed out and dissolved in 1 L ultrapure water then diluted to 2 L. Shake to mix each time before use. A freshly prepared solution should be left standing for at least 24 h hours. Shake to mix each time before use. This solution may be used for up to a month.
$\beta(K_2Cr_2O_7) = 0.6$ g/L	0.30 ± 0.01 g $K_2Cr_2O_7$ is weighed out and dissolved in 200 mL ultrapure water then diluted to 500 mL. This solution may be used for up

	to six weeks.
Phosphoric acid solution	50 mL $\beta(K_2Cr_2O_7)$ = 0.6 g/L is added to 2.5 L ortho-phosphoric acid and mixed thoroughly. This solution may be used for up to one month.
Oxidizing reagent	4 ± 0.1 g ammonium molybdate is dissolved in 400 mL ultrapure water. 500 mL $c(HNO_3)$ = 65% and 100 mL of sulfamic acid solution are added. The solution is mixed thoroughly before cooled down to room temperature and made up to 1 L with ultrapure water. This solution may be used for up to seven days.
Vanadyl sulfate solution	$\beta(VOSO_4 \cdot H_2O)$ = 2.0 g/L 2.0 ± 0.01 g vanadyl sulfate is weighed out into a 1 L volumetric flask and made up to the mark with $c(H_2SO_4)$ = 1 mol/L. This solution may be used for up to 1 month.
Ammonium fluoride $\beta(HN_4F)$ = 400 g/L	400 ± 1 g ammonium fluoride is weighed out and dissolve in ultrapure water. Then diluted to 1 L and mixed thoroughly.
Reducing solution	900 mL iron(II)sulfate solution is mixed with 300 mL sulfamic acid solution and 300 mL $\Phi(H_2SO_4)$ = 50% (v/v). This solution may be used for up to three days.

Sample preparation

For the appropriate sample preparation, see the referenced standards.

Analysis

The prepared sample is dissolved in 10 mL of $c(H_2SO_4)$ = 0.1 mol/L (the solution may need to be warmed). 2 mL of $\beta(HN_4F)$ = 400 g/L is added to the sample solution before the addition of 50 mL phosphoric acid solution. After a mixing time of 10 s, 8 mL of reducing solution is added and the sample is stirred for 150 s. Then, 10 mL oxidizing reagent is added and the solution is stirred for 3 min. After that, 50 mL vanadyl sulfate solution is added and the solution is stirred for 120 s. The solution is then titrated with $\beta(K_2Cr_2O_7)$ = 12.5 g/L until after the first equivalence point.

Parameters

Mode	MET U
Start volume	17 mL
Dosing rate	15 mL/min
Pause	10 s
Signal drift	40 mV/min
Max. waiting time	32 s
Volume increment	0.05 mL
Dosing rate	50 mL/min
Filling rate	30 mL/min
EP criterion	30 mV
EP recognition	greatest

Calculation

For the calculation of the results, see the referenced standards.

Example determination

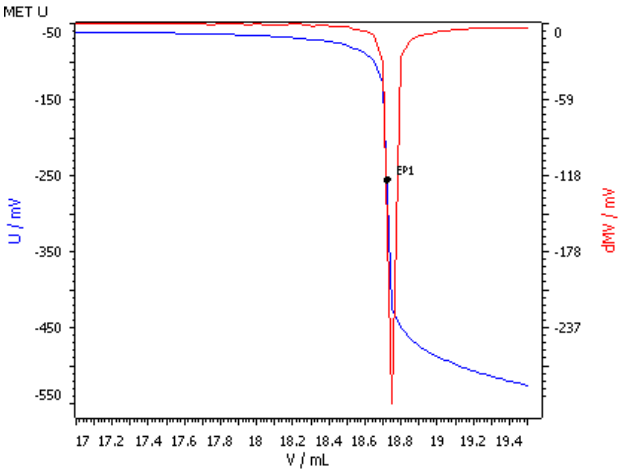


Fig. 1: Titration curve of an UF_6 pellet (blue = titration curve, red = dMV)

Comments

- The combined Pt-ring electrode is stored in c(KCl) = 3 mol/L (6.2308.020) when not in use.
- At the beginning of a series, it is recommended to place the electrode in concentrated ammonia for 30 min. This ensures that the ceramic pin diaphragm is clean and the electrode is ready for use.

References

- Davies, W., Gray, W., Talanta, 11, (1964), 1203
- ISO 7097-1:2004
  Nuclear fuel technology -- Determination of uranium in solutions, uranium hexafluoride and solids -- Part 1: Iron(II) reduction/potassium dichromate oxidation titrimetric method
- ASTM C1267-11
  Standard Test Method for Uranium by Iron (II) Reduction in Phosphoric Acid Followed by Chromium (VI) Titration in the Presence of Vanadium

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