

Voltammetric determination of aluminum

Of interest to:

General analytical laboratories; Water analysis; Pharmaceutical industry; Food analysis

B 1, 2, 4, 7, 9

Summary

This Bulletin describes a voltammetric method for the determination of aluminum in water samples, dialysis solutions, sodium chloride solutions and digestion solutions (e.g. of lyophilizates). The method utilizes the complexation of the Al^{3+} ion by Calcon (Eriochrome blue black R). The formed complex can easily be reduced electrochemically at 60 °C. The limit of quantitation depends on the purity of the reagents used and is approx. 5 µg/L.

Instruments and accessories

- 746 VA Trace Analyzer with 747 VA Stand or
- 757 VA Computrace
- Recirculation thermostat
- 6.1418.220 thermostatted measuring vessel

Electrodes

WE Multi-Mode Electrode MME
6.1246.020

RE Ag/AgCl/c(KCl) = 3 mol/L
6.0728.020 + 6.1245.010

AE Platinum
6.0343.000

Reagents

All reagents used should be of the highest purity (p.a. or «suprapur»). Only ultrapure water should be used.

- Sodium hydroxide solution, w(NaOH) = 30%, suprapur
- Acetic acid, w(CH₃COOH) = 100%, suprapur
- Methanol, puriss. p.a.
- Al^{3+} stock solution, $\beta(\text{Al}^{3+}) = 1 \text{ g/L}$ (commercially available)
- Calcon (Eriochrome blue black R), Fluka no. 45550, C.I. no. 15705, CAS 2538-85-4

Ready-to-use solutions

Buffer	c(NaOH) = 1.0 mol/L c(CH₃COOH) = 2.0 mol/L Place approx. 50 mL ultrapure water, 10 mL w(NaOH) = 30% and 11.4 mL w(CH ₃ COOH) = 100% in a 100 mL volumetric flask, fill to the mark with ultrapure water and mix.
Complexing agent	w(Calcon) = 0.05 % (0.5 g/L) in methanol This solution has to be freshly prepared every day.
Al³⁺ standard solution	$\beta(\text{Al}^{3+}) = 1 \text{ mg/L}$ This solution is prepared from the Al^{3+} stock solution by dilution with c(HCl) = 0.01 mol/L. The standard solution has to be stored in a plastic vessel and is stable for one week at most.

Sample preparation

Water samples contaminated by organic substances (surface water, waste water) have to be digested prior to the voltammetric determination. Depending on the content of organic substances (particularly surface-active substances), a UV digestion (705 UV Digester) or wet-chemical acid digestion (H₂SO₄/H₂O₂) is carried out.

Following we describe an acid digestion using an example of lyophilizates:

- 0.7 ... 0.9 g sample is mixed in a quartz Kjeldahl flask with 3 mL ultrapure water and 2 mL conc. sulfuric acid.
- Heat up the mixture carefully (formation of foam) and reduce through evaporation.
- Slowly add four portions each of 2 mL w(H₂O₂) = 30% and heat until the solution becomes clear and colorless.
- The sulfuric acid is evaporated down to a very small volume.
- After cooling down, rinse the sample solution with ultrapure water into a 100 mL volumetric flask and fill to the mark.

Analysis

Measuring solution:

20 mL sample solution at approx. pH = 2.0
 + 2 mL buffer

If necessary, adjust the pH value to 4.5 ± 0.1 with sodium hydroxide solution or acetic acid.

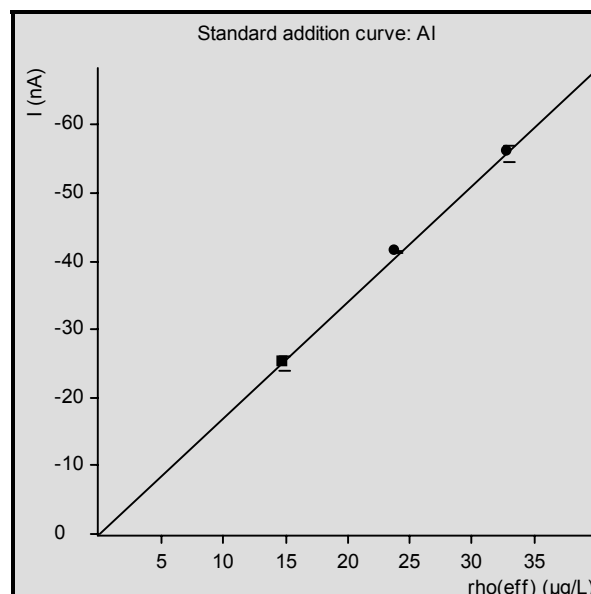
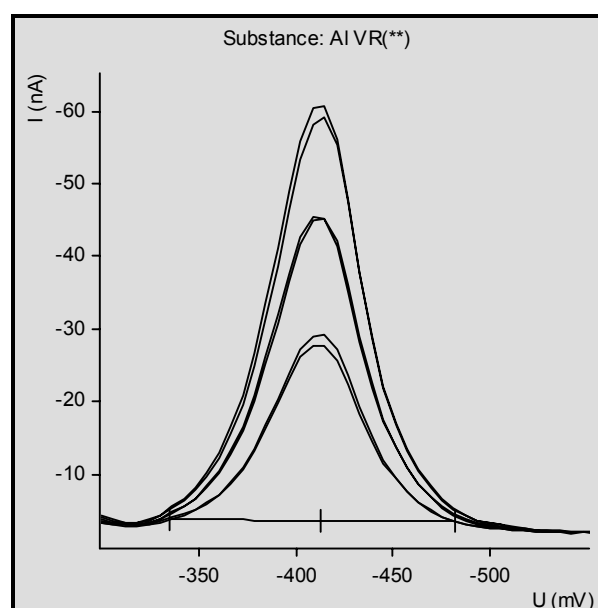
Having deaerated the measuring solution for 180 s, add 120 μL w(Calcon) = 0.05%, then record the voltammogram using the following parameters:

Working electrode	HMDE
Stirrer speed	2000 rpm
Mode	DP
Drop size	7
Purge time	300 s
Addition purge time	180 s
Deposition potential	-350 mV
Deposition time	30 s
Equilibration time	10 s
Pulse amplitude	50 mV
Start potential	-300 mV
End potential	-650 mV
Voltage step	6 mV
Voltage step time	0.4 s
Sweep rate	15 mV/s
Peak potential	-420 mV

The concentration is determined by standard addition. It is important to observe a waiting time of 3 min after each addition to allow complexation.

Example:

Determination of aluminum in drinking water



Sample volume: 20 mL

Result: 16.4 $\mu\text{g/L}$ Al^{3+}

Remarks

- The determination is to be carried out at 60 °C!
- As the voltammetric determination described is a highly sensitive method, it is necessary to determine the blank of the reagents used and take it into account when calculating the results. The blank determination is to be carried out in exactly the same way as the analysis of the sample. The same quantity of Calcon has to be added as the blank also depends on the concentration of this complexing agent.
- Al^{3+} concentrations in the ppm range are determined at the dropping mercury electrode (DME or SMDE).
- After 45 min at the most the determination should be finished, as the dyestuff may alter.
- A tenfold excess of Fe^{3+} does not yet interfere with the determination in the ppb range. However, for determinations in the ppm range the Fe^{3+} concentration should not exceed the Al^{3+} concentration. If more iron is present, it can be removed from the sample by electrolysis.
- An alternative voltammetric method for the determination of aluminum is described in Application Bulletin No. 186. With this method the interference caused by Fe^{3+} ions is far lower; however, high salt concentrations do interfere.
- If great amounts of Cu^{2+} ions (over 50-fold excess) are present, the solution turns a bright violet and the aluminum peak is suppressed.
- At pH = 4 lead is reduced at approximately the same potential as the aluminum complex. However, the lead peak is less sensitive than the aluminum peak. Interferences will only occur if Pb^{2+} is present in great excess.

Literature

- G. S. P. Ritchie, A. M. Posner, J. M. Ritchie
 The determination of trace levels of aluminum by differential pulse polarography
 Anal. Chim. Acta 117 (1980) 233–239.
- C. M. G. van den Berg, K. Murphy, J. P. Riley
 The determination of aluminum in sea water and fresh water by cathodic stripping voltammetry
 Anal. Chim. Acta 188 (1986) 177–185.
- E. Stryjewska, S. Rubel, K. Kusmierczyk
 Trace electrochemical determination of aluminum in environmental samples
 Fresenius Z. Anal. Chem. 334 (1989) 627.
- L. Chiang, B. D. James, R. J. Magree
 Adsorptive stripping voltammetry of some trace elements in biological samples. Nickel, arsenic, aluminum and selenium
 Mikrochim. Acta (1989) 149–152.

Method for the determination of aluminum with the 746 VA Trace Analyzer

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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB131 .mth OPERATION SEQUENCE
Title : Determination of aluminum. AB131
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	Instructions	t/s	Main parameters	Auxiliary parameters
1	DOS/M		V.added 2.000 mL	
2	SMPL/M		V.fraction mL	V.total L
3	PURGE			
4	STIR	180.0	Rot.speed 2000 /min	
5	DOS>M		Soln.name ErioR	V.add 0.120 mL
6	PURGE	300.0		
7	(ADD			
8	PURGE			
9	STIR	180.0	Rot.speed 2000 /min	
10	OPURGE			
11	SEGMENT		Segm.name csv	
12	PURGE			
13	ADD>M		Soln.name Al-std	V.add 0.200 mL
14	ADD)2			
15	END			

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Method: AB131 SEGMENT
                csv
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	Instructions	t/s	Main parameters	Auxiliary parameters
1	(REP			
2	STIR	5.0	Rot.speed 2000 /min	
3	HMDE		Drop size 7	Meas.cell normal
4	DPMODE		U.ampl -50 mV	t.meas 20.0 ms
			t.step 0.40 s	t.pulse 40.0 ms
5	MEAS	30.0	U.meas -350 mV	
6	OSTIR	10.0		
7	SWEEP	24.8	U.start -300 mV	U.step 6 mV
			U.end -650 mV	Sweep rate 15 mV/s
			U.standby mV	
8	OMEAS			
9	REP)1			
10	STIR		Rot.speed 2000 /min	
11	END			

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Method: AB131 SUBSTANCES
                Al - csv
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Recognition		Display / Plot	
U.verify	-420 mV	I.scale	auto
U.tol (+/-)	50 mV	U.div	50.00 mV/cm
U.width min	10 mV	U.begin	-300 mV
U.width max	400 mV	U.end	-550 mV
I.threshold	100 pA		

Baseline		Evaluation	
Type	linear	Mode	VA
Scope	whole	Quantity	I.peak
dU.front	auto	Sign. digits	4
S.front	auto		
dU.rear	auto		
S.rear	auto		

Calibration	2000-11-28 17:11:34		Coefficients	
Technique	std.add.		Y.reg	-2.529e-08
Curve type	linear		Slope	-0.001702
			Nonlin.	
			Mean dev.	9.781e-10

	Additions			
Soln.name	Al-std			
Mass conc.	1 mg/L	g/L	g/L	g/L
Range min	g/L	g/L	g/L	g/L
Range max	g/L	g/L	g/L	g/L
M.conc./cm	g/L	g/L	g/L	g/L
Method: AB131	CALCULATION			
	max. 15 lines			

Quantity	Formula (R##, C##, A##)		Res.unit	Sig.dig.
Al	R1000=MC:Al		#g/L	5

Full report of the determination of aluminum in drinking water

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====					
Determ.	: 06040939	User:	Date: 1999-06-04		
Modified	: 1999-06-04 09:40:38	Run : 0	Time: 09:39:28		
Sample table:	-				
Pos.	Ident.1/S1	Ident.2/S2	Ident.3/S3	Method.call	Sample size/S0
	tap water				20 mL

Method	: AB131				
Title	: Determination of aluminum. AB131				
Remark1	: Determination of Al at 60 °C				
Remark2	: 20mL sample + 2mL buffer --> pH 4.5 + 120µL Erio R (0.5 g/L)				

Substance	: Al		Comments		
Mass conc.:	16.44 ug/L	Mass	: 328.8 ng	-----	
MC.dev.:	1 ug/L (6.08%)	Add.mass	: 200 ng		
Cal.dev.:	-	V0.sample:	: 20 mL		
	VR	U/mV	I/nA	I.mean	Std.dev.
	00	-412	-25.69	-24.98	0.9975
	01	-412	-24.27		
	10	-411	-41.00	-40.94	0.0863
	11	-413	-40.87		
	20	-413	-53.86	-54.75	1.258
	21	-413	-55.64		
Substance	Techn.	Y.reg/offset	Slope	Nonlin.	Mean deviat.
Al	std.add.	-2.529e-08	-0.001702		9.781e-10
SOLUTIONS					
max. 40					

Soln.name	Pos.	Std.subst.	Mass conc.	Remark	

C#	Workg.com.var	Remark			

Final results			+/- Res.dev.	%	Comments
	Al =	16.439 ug/L	1.00	6.08	-----