

## Polarographic determination of nitrate in water samples, soil and plant extracts, vegetable juices, meat and sausages, fertilizers, liquid manure, etc.

Of interest to:

General analytical laboratories; Water, waste water, environmental protection; Food, beverages; Biochemistry, biology; Fertilizers, base materials, explosives

B 1, 2, 7, 8, 11

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### Summary

The photometric determination of nitrate is limited by the fact that the respective methods (salicylic acid, brucine, 2,6-dimethyl phenol, Nessler's reagent after reduction of nitrate to ammonium) are subject to interferences. The direct potentiometric determination using an ion-selective nitrate electrode causes problems in the presence of fairly large amounts of chloride or organic compounds with carboxyl groups.

The polarographic method, on the other hand, is not only more rapid, but also practically insensitive to chemical interferences, thus ensuring more accurate results. The limit of quantitation depends on the matrix of the sample and is approximately 1 mg/L.

### Instruments and accessories

- 746 VA Trace Analyzer with 747 VA Stand or
- 757 VA Computrace

### Reagents

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

- Sulfuric acid,  $w(\text{H}_2\text{SO}_4) = 96\%$
- Phenol, puriss. p.a.
- 2-Nitrophenol, puriss. p.a., CAS 88-75-5
- Zinc acetate  $\text{Zn}(\text{CH}_3\text{COO})_2$
- Potassium hexacyanoferrate(II)  $\text{K}_4\text{Fe}(\text{CN})_6$

### Ready-to-use solutions

Zinc acetate solution	$w[\text{Zn}(\text{CH}_3\text{COO})_2] = 30\%$
Potassium hexacyanoferrate(II) solution	$w[\text{K}_4\text{Fe}(\text{CN})_6] = 15\%$
Standard addition solution	$\rho(2\text{-nitrophenol}) = 1 \text{ g/L}$ in water

### Sample preparation

- Ground, drinking and surface water can be analyzed directly; the same applies to solutions or extracts of fertilizers.
- Samples containing insoluble organic compounds (e.g. vegetable juices, waste water and slurries made from plant or foodstuff samples) are diluted with dist. water if necessary and centrifuged in order to obtain a clear solution, which is then used for the analysis.
- For meat and sausages the procedure is as follows:  
To 10 g sample cut into small pieces add 100 mL dist. water and mix for 5 min in a high frequency mixer, then allow to stand for 1 h in a water bath at 90 °C. Add 2 mL  $w[\text{Zn}(\text{CH}_3\text{COO})_2] = 30\%$ , then 2 mL  $w[\text{K}_4\text{Fe}(\text{CN})_6] = 15\%$  and mix (Carrez precipitation). Filter the mixture first through a paper filter, then through a membranous filter (0.45 µm). The obtained clear solution is used for the analysis. (Determination of nitrite in this solution is also possible, see Application Bulletin No. 127.)

## Analysis

Place 1 mL sample solution (which may contain 1 ... 200 mg/L N) in the polarographic vessel and add 1 mL liquid phenol as well as 4 mL  $w(\text{H}_2\text{SO}_4) = 96\%$  under stirring. After cooling down, carefully add 4 mL dist. water, stirring again. The solution is then left to cool down to room temperature.

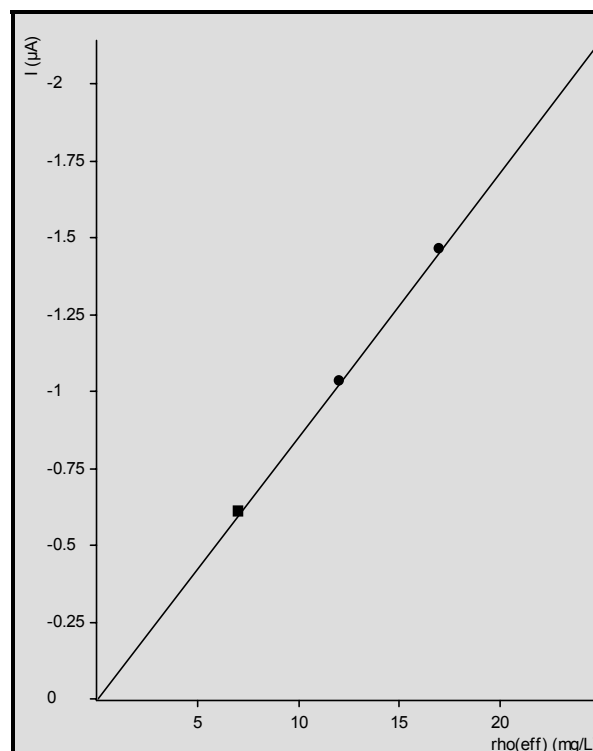
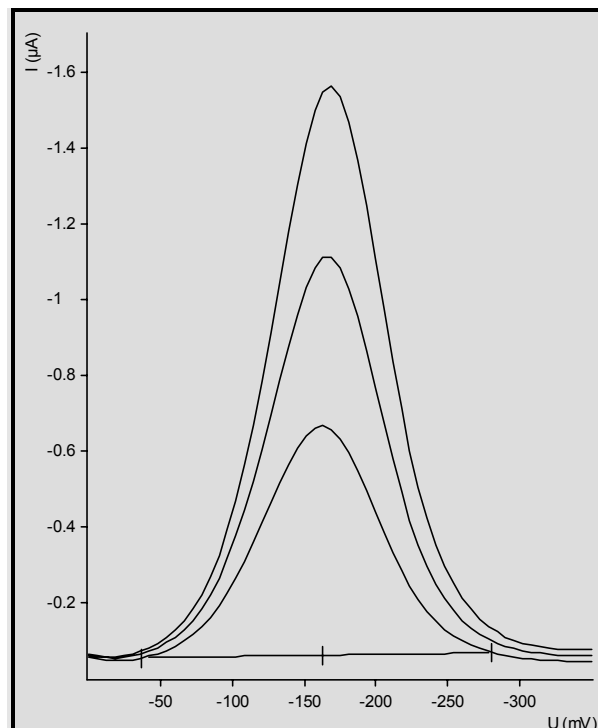
The polarogram is recorded at the DME using the following parameters:

Working electrode	DME
Stirrer speed	2000
Mode	DP
Purge time	300 s
Equilibration time	5 s
Pulse amplitude	50 mV
Start potential	0 mV
End potential	-350 mV
Voltage step	6 mV
Voltage step time	0.6 s
Sweep rate	10 mV/s
Peak potential	-170 mV

The concentration is determined by standard addition of 2-nitrophenol or by means of nitrate standard subjected to the same treatment.

## Example:

### Determination of nitrate in drinking water



Sample volume: 1 mL

**Result:** 70.7 mg/L  $\text{NO}_3^-$

## Remarks

- The method will not work in solutions containing proteins. These must first be put through the precipitation procedure described above.
- If the nitrite content is also of interest, this is first oxidized in a second sample with  $\text{H}_2\text{O}_2$  to nitrate and then determined. It is also possible to determine nitrite directly according to Application Bulletin No. 127.
- The method has been successfully tested in drinking and mineral water, inlet and outlet of waste water treatment plants, vegetable juices (tomato, potato, beetroot, sauerkraut), spinach, meat and sausages and aerated liquid manure.

## Literature

- M. Bartik, J. Kupka  
Collect. Czechoslov. Chem. Commun. 25 (1960) 3356  
Ref.: Fresenius Z. Anal. Chem. 183 (1961) 234.
- Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung  
Verlag Chemie GmbH, Weinheim/Bergstrasse.

**Appendix**

**Method of the determination of nitrate with the 746 VA Trace Analyzer**

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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB070 .mth OPERATION SEQUENCE
Title : Determination of nitrate
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	Instructions	t/s	Main parameters	Auxiliary parameters
1	DOS/M		V.added 9.000 mL	
2	SMPL/M		V.fraction mL	V.total L
3	PURGE			
4	STIR	300.0	Rot.speed 2000 /min	
5	(ADD			
6	PURGE			
7	STIR	30.0	Rot.speed 2000 /min	
8	OPURGE			
9	OSTIR	5.0		
10	SEGMENT		Segm.name Nitrate	
11	ADD>M		Soln.name NO3std	V.add 0.050 mL
12	ADD)2			
13	END			

```

Method: AB070 SEGMENT
Nitrate
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	Instructions	t/s	Main parameters	Auxiliary parameters
1	DME			
2	DPMODE		U.ampl -50 mV	t.meas 20.0 ms
			t.step 0.60 s	t.pulse 40.0 ms
3	SWEEP	37.2	U.start 0 mV	U.step 6 mV
			U.end -350 mV	Sweep rate 10 mV/s
4	OMEAS		U.standby mV	
5	END			

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Method: AB070 SUBSTANCES
NO3 - Nitrate
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Recognition		Display / Plot	
U.verify	-170 mV	I.scale	auto
U.tol (+/-)	50 mV	U.div	50.00 mV/cm
U.width min	10 mV	U.begin	mV
U.width max	200 mV	U.end	mV
I.threshold	250 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		Coefficients	
Calibration	2000-08-22 13:54:48	Y.reg	-6.047e-07
Technique	std.add.	Slope	-8.55e-05
Curve type	linear	Nonlin.	
		Mean dev.	3.178e-09

Additions				
Soln.name	NO3std			
Mass conc.	1 g/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

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Method: AB070 CALCULATION
max. 15 lines
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Quantity	Formula (R##, C##, A##)	Res.unit	Sig.dig.
NO3	R1000=MC:NO3	#g/L	5

