

Polarographic determination of trace amounts of molybdenum in water

Of interest to:

General analytical laboratories, Water, Trace analysis
B 1, 2, 9

Summary

Molybdenum is an essential trace element for plant growth. Since it occurs in natural waters only in trace amount, a very sensitive method of determination is needed. With the aid of the following polarographic method, it is possible to determine $5 \cdot 10^{-10}$ mol/L resp. 50 ng/L.

The principle of the method is based on the reaction between the molybdate ion MoO_4^{2-} and the complexing agent 8-hydroxy-7-iodo-quinoline-5-sulfonic acid (H_2L) to form a $\text{MoO}_2\text{L}_2^{2-}$ complex, which is adsorbed on the mercury electrode. The adsorbed Mo(VI) is reduced electrochemically to the Mo(V) complex. The hydrogen ions present in the solution oxidise again spontaneously to form the Mo(VI) complex, which is thus newly available for electrochemical reduction. This catalytic reaction is the reason for the high sensitivity of the method.

Apparatus and accessories

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

Sample preparation

Organic matter often interferes with voltammetric determinations and therefore sample solutions usually have to be digested.

- Ground water, sea water, mineral waters and drinking waters can usually be analysed without pretreatment.
- Low polluted waste waters can be digested with the 705 UV Digester.
Add 50 μL hydrogen peroxide solution $w(\text{H}_2\text{O}_2) = 30\%$ and 10 μL hydrochloric acid $w(\text{HCl}) = 30\%$ to 10 mL acidified sample ($\text{pH} = 2$) and irradiate for 60 minutes at 90°C .
- Samples with organic matter (foods, pharmaceuticals etc.) must be digested.
 - High-pressure asher
 - Microwave digestion
Both techniques oxidise the sample in a closed digestion vessel by means of a mixture of concentrated mineral acids.
 - Open wet digestion with H_2SO_4 and H_2O_2 According to Application Bulletin 113.

Reagents

All used reagents must be of purest quality possible (p.a. or suprapur). Only high purity water is used to prepare the solutions.

- 8-hydroxy-7-iodo-quinoline-5-sulfonic acid; ferron (e.g. Fluka No. 55370), CAS 547-91-1
- Sulphuric acid, suprapur, $w(\text{H}_2\text{SO}_4) = 96\%$
- Potassium chloride, suprapur, CAS 7447-40-7
- Mo standard stock solution: $\beta(\text{Mo}^{6+}) = 1$ g/L (commercially available)

Ready-to-use solutions:

Diluted sulphuric acid	$c(\text{H}_2\text{SO}_4) = 0.1$ mol/L
	<i>5.5 mL sulphuric acid are diluted to 1 L with ultrapure water.</i>
Reagent solution	$c(8\text{-hydroxy-7-iodo-quinoline-5-sulfonic acid}) = 2 \cdot 10^{-4}$ mol/L, $c(\text{KCl}) = 0.7$ mol/L $c(\text{H}_2\text{SO}_4) = 0.1$ mol/L
	<i>Dissolve 35 mg 8-hydroxy-7-iodo-quinoline-5-sulfonic acid in 450 mL diluted sulphuric acid. Add 26.1 g potassium chloride and fill up to 500 mL with diluted sulphuric acid.</i>
Molybdenum standard solution	$\beta(\text{Mo}^{6+}) = 100$ $\mu\text{g/L}$
	<i>Prepare more diluted standard solutions $\beta(\text{Mo}^{6+}) = 10 \dots 200$ $\mu\text{g/L}$ through dilution of the 1 g/L molybdenum standard stock solution with sulphuric acid 0.1 mol/L.</i>

Analysis

10 mL (diluted) sample
 + 2 mL reagent solution

The polarogram is recorded under the following conditions.

Working electrode	SMDE
Stirrer speed	2000 rpm
Mode	DP
Purge time	300 s
Equilibration time	5 s
Pulse amplitude	50 mV
Start potential	-680 mV
End potential	-1180 mV
Voltage step	6 mV
Voltage step time	0.6 s
Sweep rate	10 mV/s
Peak potential	-1000 mV

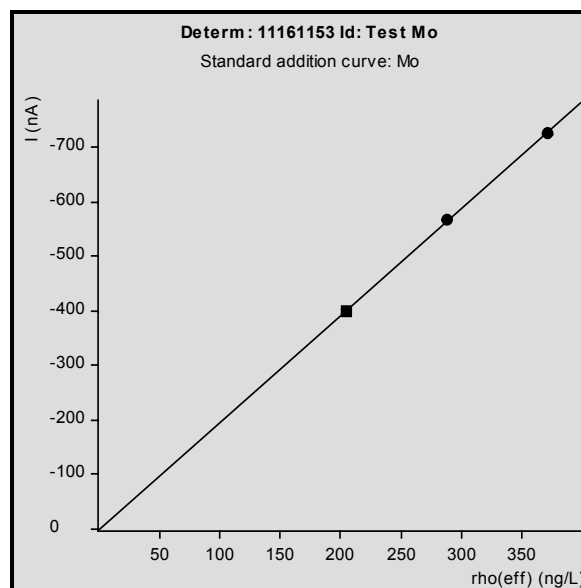
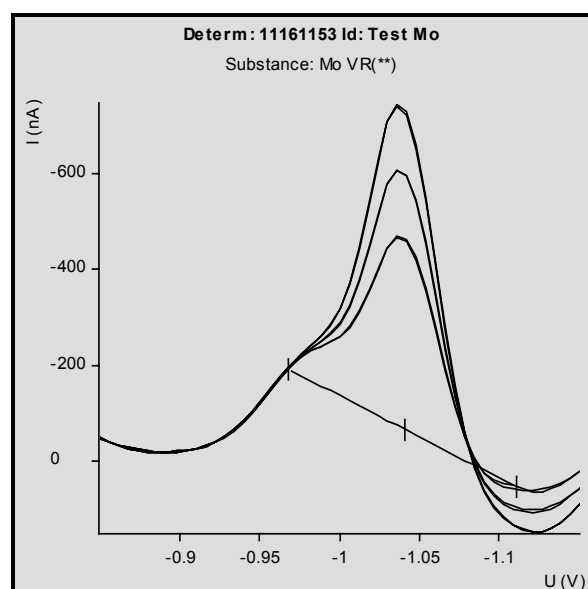
The concentration is determined by standard addition.

For an accurate determination of the concentration, the chemical blank value must be taken into consideration. To do this, determine the molybdenum concentration of 10 mL high purity water and 2 mL reagent solution under the same conditions as is given for the sample.

Example

Molybdenum determination in drinking water with the 746 VA Trace Analyzer

(the shoulder at - 980 mV is caused by approx. 250 µg/L Zn)



Sample volume 10 mL

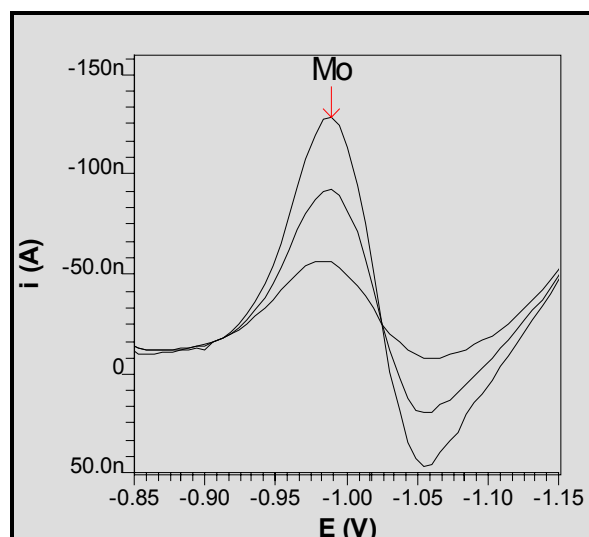
Result 245 ng/L Mo

Remarks

Reduction of the reagent's blank value

For determinations in which an extremely low chemical blank value is desired, the self-synthesising 5-sulfo-7-nitro-hydroxyquinoline (monohydrate) can be used instead of the commercially available 8-hydroxy-7-iodo-quinoline-5-sulfonic acid.

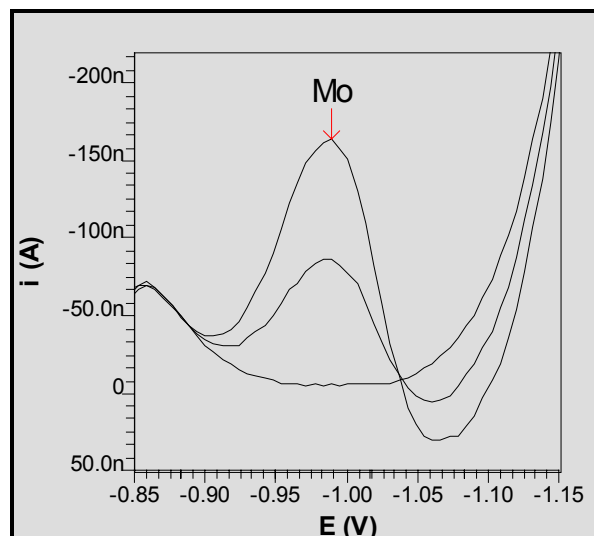
Blank value 8-hydroxy-7-iodo-quinoline-5-sulfonic acid



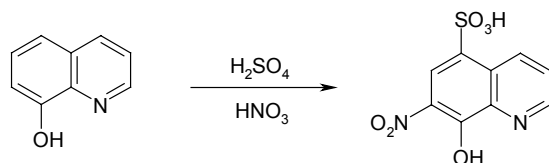
Sample volume 10 mL

Result 22 ng/L Mo

Blank value 7-nitro-8-hydroxyquinoline-5-sulfonic acid



Synthesis of the 7-nitro-8-hydroxyquinoline-5-sulfonic acid monohydrate



- 8-Hydroxyquinoline, CAS 148-24-3
- Oleum (fuming sulphuric acid, 30 % SO₃), CAS 8014-96-7
- Nitric acid, w(HNO₃) = 65 %

Dissolve 4.335 g (0.03 mol) 8-hydroxyquinoline in 50 mL oleum at 50 °C. The solution is cooled to 0 °C and 7 mL nitric acid are added dropwise with vigorous stirring and cooling.

Stirring is continued for 15 min and the solution is then poured onto 450 g crushed ice. The by-product, 5,7-dinitro-8-hydroxyquinoline-5-sulfonic acid monohydrate, is precipitated and filtered off.

The filtrate is stored for two days at -21 °C. After this time, 7-nitro-8-hydroxyquinoline-5-sulfonic acid monohydrate is precipitated. The precipitate is filtered off, washed several times with small amounts of ice water and finally recrystallised in water. It is dried in vacuum at 1 Pa and 23 °C.

Interferences through other ions

Experiments have shown that potential interfering ions (PII) such as Zn²⁺, Co²⁺, Mn²⁺, Ca²⁺, Al³⁺ and TI⁺ cause no interference at molar ratios (PII) / Mo⁶⁺ ≤ 10⁺³.

Tungsten W(VI), on the other hand, exhibits practically the same electrochemical behaviour as molybdenum and is hence determined at the same time. With molar ratios W⁶⁺ / Mo⁶⁺ ≤ 10, the masking of tungsten with 0.001 mol/L tartaric acid is complete and there is no interference with the molybdenum determination. With a greater percentage of tungsten, 0.01 mol/L tartaric acid is needed. The sensitivity of the Mo determination is then lowered to app. 37% of the original value (without tartaric acid addition).

Literature

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Anal. Chim. Acta 116(1980), 323 – 333
- Bosserman P., Sawyer D.T., Page A.L.
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- Lanza P., Ferri D., Buldini P.A.
Analyst 105(1980), 379 - 385
- Metrohm Application Bulletin 132

Appendix

Example of a molybdenum determination in drinking water with the 746 VA Trace Analyzer

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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Determ.      : 11161153          User: zu          Date: 1999-11-16
Modified     : 1999-11-16 12:02:35 Run : 4             Time: 11:53:35
Sample table: -
-----
  Pos.  Ident.1/S1  Ident.2/S2  Ident.3/S3  Method.call  Sample size/S0
      Test Mo
-----
Method : AB146
Title  : Determination of Molybdenum in Waters. AB146
Remark1: 10 mL tap water + 2 mL reagent solution
Remark2 :
-----
Substance : Mo                      Comments
Mass conc.: 245.6 ng/L              Mass      : 2.456 ng
MC.dev.   : 4.12 ng/L (1.68%)      Add.mass  : 1 ng
Cal.dev.  : -                      V0.sample: 10 mL
-----
      VR  U/mV  I/nA  I.mean  Std.dev.  I.delta  Comments
-----
      00 -1042 -396.3 -399.0  3.886     -         crit. front ovlp.
      01 -1042 -401.8 -399.0  3.886     -         crit. front ovlp.
      10 -1041 -561.8 -561.7  0.1205   -162.7
      11 -1041 -561.6 -561.7  0.1205   -162.7
      20 -1040 -711.8 -713.2  1.913    -151.5
      21 -1040 -714.5 -713.2  1.913    -151.5
-----
Substance  Techn.  Y.reg/offset  Slope  Nonlin.  Mean deviat.
-----
Mo         std.add.  -4.004e-07  -1.956  -         3.322e-09
-----
C#  Workg.com.var  Remark
-----
Final results          +/-  Res.dev.  %  Comments
-----
Mo = 245.63 ng/L      4.12  1.68

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Method for the molybdenum determination with the 746 VA Trace Analyzer

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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB146 .mth          OPERATION SEQUENCE
Title : Determination of Molybdenum in Waters. AB146
-----
Instructions  t/s  Main parameters  Auxiliary parameters
-----
1  DOS>M
2  SMPL>M      Soln.name  reag_sol  V.add      2.000 mL
3  REM         V.fraction  mL        V.total    L
4  PURGE      10 mL sample + 2 mL reagent solution
5  STIR       300.0  Rot.speed   2000 /min
6  (ADD
7  STIR       30.0   Rot.speed   2000 /min
8  PURGE
9  SEGMENT    Segm.name  csv
10 ADD>M     Soln.name  Mo-std    V.add      0.100 mL
11 ADD)2
12 END
Method: AB146          SEGMENT
                        csv
-----
Instructions  t/s  Main parameters  Auxiliary parameters
-----
1  0PURGE
2  0STIR      5.0
3  (REP
4  SMDE      Drop size    6
5  DPMODE    U.ampl      -50 mV      t.meas     20.0 ms
              t.step      0.60 s     t.pulse    40.0 ms
6  SWEEP     52.2  U.start      -680 mV     U.step     6 mV
              U.end       -1180 mV    Sweep rate  10 mV/s
              U.standby   mV
7  OMEAS
8  REP)1
9  PURGE
10 STIR      Rot.speed   2000 /min
11 END

```