Metrohm

Application Bulletin 146/3 e

Determination of trace amounts of molybdenum (or tungsten) in water by polarography

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. Using 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 $MoO_2L_2^{2-}$ 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 oxidize Mo(V) 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.

Tungsten W(VI) exhibits practically the same electrochemical behavior as molybdenum, but is not described in detail in this Application Bulletin.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode

Electrodes

WE	Multi-Mode Electrode pro Mercury drop capillary	6.1246.120 6.1226.030 or 6.1226.050
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L) Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.0728.x20 6.1245.010
AE	Pt rod electrode	6.0343.x00

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*).

- 8-hydroxy-7-iodo-quinoline-5-sulfonic acid, CAS 547-91-1
- Sulfuric acid, for trace analysis*, w(H_2SO_4) = 96 %, CAS 7664-93-9
- Potassium chloride, for trace analysis*, CAS 7447-40-7
- Mo standard stock solution: β(Mo^{6+}) = 1 g/L (commercially available)
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

* e.g., Merck suprapur®, Honeywell Fluka TraceSelect® or equivalent

Solutions

Diluted sulfuric acid	c(H_2SO_4) = 0.1 mol/L 5.5 mL sulfuric acid are diluted to 1 L with ultrapure water.
Reagent solution	c(8-hydroxy-7-iodo-quinoline-5-sulfonic acid) = 2·10-4 mol/L c(KCl) = 0.7 mol/L c(H_2SO_4) = 0.1 mol/L Dissolve 35 mg 8-hydroxy-7-iodo-quinoline-5-sulfonic acid in 450 mL diluted sulfuric acid. Add 26.1 g potassium chloride and fill up to 500 mL with diluted sulfuric acid.

Standard solution

Molybdenum standard solution	β(Mo^{6+}) = 100 µg/L Prepare more diluted standard solutions β(Mo^{6+}) = 10 ... 200 µg/L through dilution of the 1 g/L molybdenum standard stock solution with sulfuric acid 0.1 mol/L.

Sample preparation

- Ground water, sea water, mineral waters and drinking waters can usually be analyzed without pretreatment.

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

- Low polluted waste waters can be digested with the 909 UV Digester.
  - Add 50 µL hydrogen peroxide solution w(H_2O_2) = 30% and 10 µL hydrochloric acid w(HCl) = 30% to 10 mL acidified sample (pH = 2) and irradiate for 90 minutes at 90°C.
- Samples with organic matter (foods, pharmaceuticals etc.) must be digested.
  - High-pressure asher
  - Microwave digestion
  - Both techniques oxidize 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.

Analysis

Measuring solution

10 mL (diluted) sample

2 mL reagent solution

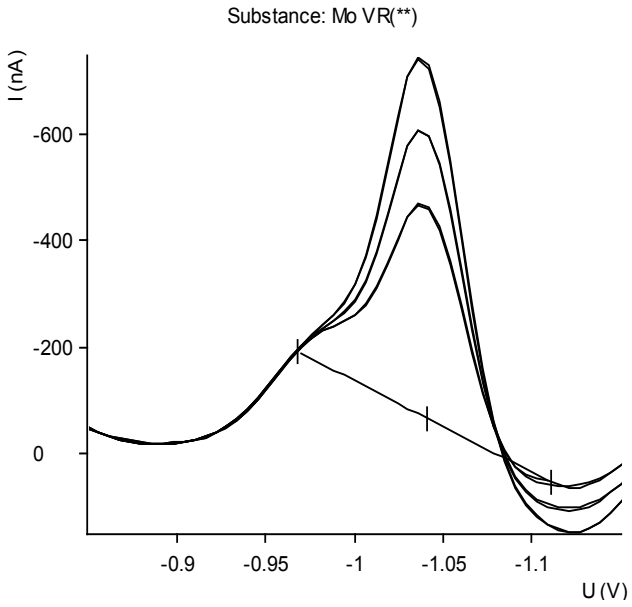
The concentration is determined by standard addition.

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.

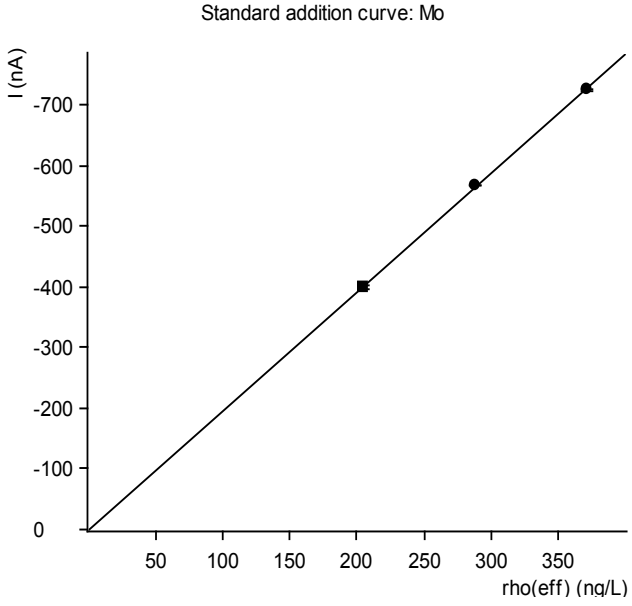
Parameters

Voltammetric	
Electrode operating mode	SMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	5 s
Sweep	
Start potential	-0.68 V
End potential	-1.18 V
Potential step	0.006 V
Potential step time	0.6 s
Sweep rate	0.01 V/s
Pulse amplitude	0.05 V
Substance	
Name	Mo
Characteristic potential	-1.0 V

Example



The shoulder at - 980 mV is caused by approx. 250 µg/L Zn



Results

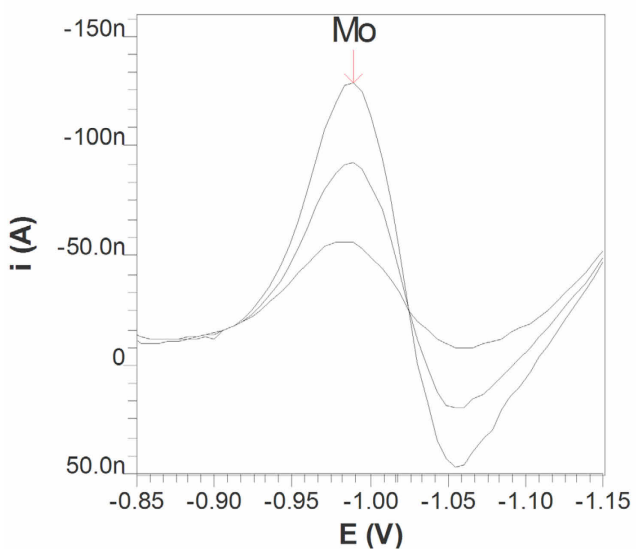
Sample	Drinking water
Sample size	10.0 mL
β(Mo)	245 ng/L

Comments

Reduction of the reagents blank

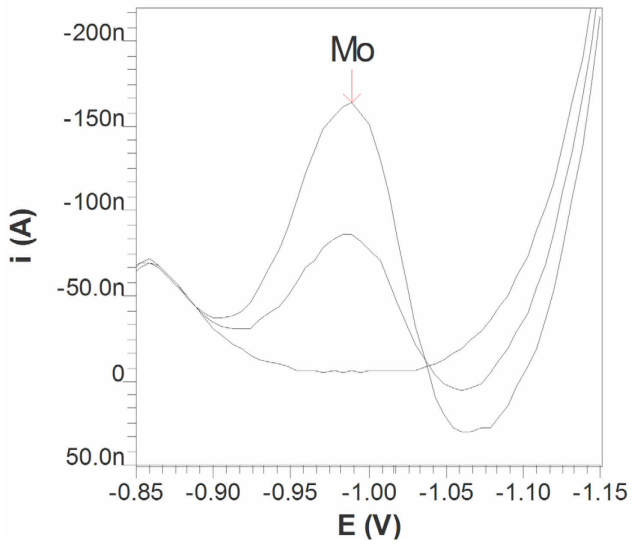
For determinations in which an extremely low chemical blank value is desired, the self-synthesizing 5-sulfo-7-nitro-hydroxyquinoline (monohydrate) can be used instead of the commercially available 8-hydroxy-7-iodo-quinoline-5-sulfonic acid.

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

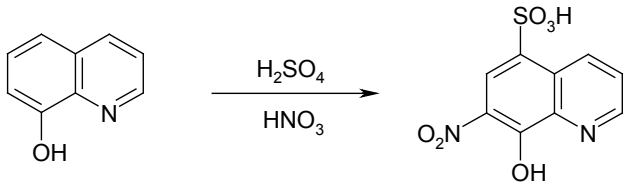


Sample volume	10 mL
Result	22 ng/L Mo

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 % SO_3), CAS 8014-96-7
- Nitric acid, w(HNO_3) = 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 recrystallized in water. It is dried in vacuum at 1 Pa and 23°C.

Interferences from other ions

Experiments have shown that potential interfering ions (PII) such as Zn^{2+}, Co^{2+}, Mn^{2+}, Ca^{2+}, Al^{3+} and Tl^{+} cause no interference at molar ratios (PII) / $Mo^{6+} \leq 10^{+3}$.

Tungsten W(VI), on the other hand, exhibits practically the same electrochemical behavior as molybdenum and is hence determined at the same time. With molar ratios W^{6+} / $Mo^{6+} \leq 10$, 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).

References

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  Microchimica Acta (Wien), 1977/II, 569
- Edmonds T.E.
  Anal. Chim. Acta 116(1980), 323 – 333

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  Anal. Chem. 50(1978), 1300 - 1303
- Lanza P., Ferri D., Buldini P.A.
  Analyst 105(1980), 379 - 385
- Metrohm Application Bulletin 132

Appendix

Report for the example determination of a molybdenum determination in drinking water

```
================== 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                                                        10 mL
--------------------------------------------------------------------------------
 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                             crit. front ovlp.
              10   -1041  -561.8  -561.7   0.1205   -162.7
              11   -1041  -561.6
              20   -1040  -711.8  -713.2    1.913   -151.5
              21   -1040  -714.5

 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
```

Method print for the determination of molybdenum

```
================== 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               Soln.name   reag_sol       V.add         2.000 mL
 2    SMPL>M              V.fraction          mL     V.total              L
 3    REM                 10 mL sample + 2 mL reagent solution
 4    PURGE
 5    STIR          300.0 Rot.speed      2000 /min
 6    (ADD
 7      STIR              Rot.speed      2000 /min
 8      PURGE       30.0
 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
 7      0MEAS             U.standby           mV
 8    REP)1
 9    PURGE
10    STIR              Rot.speed      2000 /min
11    END
```