Application Bulletin

Of interest to:	General laboratories, Metals, Galvanic industry Fertilisers, Environmental protection laboratories	B 1, 2, 10, 11, 15

Voltammetric determination of molybdenum in strongly ferruginous materials

Summary

In this Bulletin a method is described for the determination of molybdenum also in steels and other strongly ferruginous substances. By means of catalytic polarography Mo(VI) is determined at the dropping mercury electrode. The determination limit lies at approx. 10 µg/L Mo(VI).

Apparatus and accessories

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

Reagents

All of the used reagents must be of purest quality possible (p.a. or suprapur) and only high purity water should be used.

- Sulphuric acid, w(H_2SO_4) = 98 %
- Nitric acid, w(HNO_3) = 65 %
- Phosphoric acid, w(H_3PO_4) = 85 %
- Perchloric acid, w ($HClO_4$) = 70 %
- Hydrochloric acid, w(HCl) = 37%
- Ammonium nitrate, puriss p.a. , CAS 6484-52-2
- Cation exchanger:
  strongly acid, such as e.g. Dowex 50, Amberlite IR-120 etc.
- Molybdenum(VI) standard stock solution 1000 mg/L, commercially available

Ready to use solutions

- Nitric acid diluted, c(HNO_3) = 0.5 mol/L
- Hydrochloric acid, diluted, c(HCl) = 4 mol/L
- Acid mixture (for dissolving steel):
  Carefully mix 100 mL each of conc. H_2SO_4, H_3PO_4 and $HClO_4$ with 300 mL dist. water.
- Molybdenum standard ß(Mo) = 10 mg/L

Sample preparation

Digestion

Steel samples

- Samples containing more than 1 % molybdenum may be dissolved directly in the acid mixture described in „Reagents“ above. For further details, see the original paper: Analyst 105(1980), 379-385.
- For samples containing less than 1 % Mo, use the following procedure: Place 50...500 mg sample (corresponding to 5....500 µg Mo) in a beaker, add 12 mL dist. water and 6 mL conc. nitric acid. When the reaction is finished, boil for a few minutes, allow to cool, rinse into a 50 mL volumetric flask and fill up to the mark with distilled water.

Sewage sludge and similar samples

The following description applies to a sample of sewage sludge containing 62.3 g iron per kg dry sludge.

About 1 g of dry sludge is weighed accurately and placed in a Kjeldahl flask, to which 2 mL each conc. sulphuric acid and nitric acid are added. The mixture is heated on a Bunsen burner until it slowly carbonises, whereupon a further 5 mL nitric acid is added. Heating is continued until no more nitroso-gases are given off. Additions of nitric acid are repeated until all organic matter is completely destroyed. Afterwards the solution is heated until practically all the sulphuric acid has evaporated. Add 5 mL dist. water and evaporate again. Repeat this operation. Allow the solution to cool, add 10 mL dist. water and allow to boil for a short while. After cooling, the solution is rinsed into a 100 mL volumetric flask with dist. Water and filled up to the mark. A blank control sample is prepared with identical quantities of reagents. The following elements can be determined in the digestion solution: Cd Co, Cr, Cu, Fe, Ni, Pb, Se and Zn (see also Application Bulletins 113, 114, 116 and 117).

Preparation

Solutions containing more than 10 mg/L Fe(III) have to be passed through a cation exchanger prior to the voltammetric measurement.

Treatment with ion exchanger

Fill a chromatographic column 20 cm long and 1 cm in diameter with cation exchanger and convert this to the „H“ state with $c(HNO_3)$ = 0.5 mol/L. Now allow 10...40 mL digestion solution to percolate through the ion exchanger and run the eluate into a 200 mL volumetric flask. Continue rinsing the column with $c(HNO_3)$ = 0.5 mol/L until the flask is filled up to the mark. Mix the contents of the flask thoroughly (the ion exchanger can be regenerated by pouring through 400 mL c(HCl) = 4 mol/L).

Analysis

Measuring solution:

5 mL eluate
+ 5 mL water
+ 1.6 g ammonium nitrate (2 mol/L)

The polarogram is recorded with following parameters:

working electrode	SMDE
drop size	4
stirrer speed	2000 rpm
mode	DP
purge time	300 s
equilibration time	10 s
pulse amplitude	50 mV
start potential	150 mV
end potential	-450 mV
voltage step	10 mV
voltage step time	0.4 s
sweep rate	25 mV/s
peak potential	-170 mV

The concentration is determined by means of the standard addition method.

Literature

- Lanza P., Ferri D., Buldini P.L.
  Differential-pulse Polarographic Determination of Molybdenum in Steel.
  Analyst 105, (1980) 379-385

Figures

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================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB132   .mth         OPERATION SEQUENCE
 Title : Determination of Mo at SMDE. AB 132
-------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------- -------------------------
 1    REM                  10 mL sample + 1.6 g ammonium nitrate
 2    SMPL/M               V.fraction          mL    V.total              L
 3    PURGE
 4    STIR          300.0  Rot.speed      2000 /min
 5    (ADD
 6      STIR               Rot.speed      2000 /min
 7      PURGE        30.0
 8      SEGMENT            Segm.name   pol
 9      ADD>M              Soln.name   Mo-std         V.add         0.020 mL
10    ADD)2
11    END

 Method: AB132                SEGMENT
                               pol
-------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------- -------------------------
 1    0PURGE
 2    0STIR         10.0
 3    (REP
 4      SMDE               Drop size         4
 5      DPMODE             U.ampl          -50 mV    t.meas         30.0 ms
                           t.step         0.40 s     t.pulse        40.0 ms
 6      SWEEP        25.6  U.start         150 mV    U.step           10 mV
                           U.end          -450 mV    Sweep rate       25 mV/s
 7      0MEAS              U.standby           mV
 8    REP)1
 9    PURGE
10    STIR               Rot.speed      2000 /min
11    END

  Method: AB132                SUBSTANCES
                              Mo       - pol
-------------------------------------------------------------------------------

      Recognition                           Display / Plot
      --------------------------            ----------------------------
      U.verify          -171 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        200 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   2000-11-29 19:46:06         Coefficients
  ------------------------------------      -------------------------
  Technique     std.add.                    Y.reg        -4.701e-09
  Curve type    linear                      Slope        -0.0002198
                                            Nonlin.
                                            Mean dev.     4.686e-11

                Additions
                ------------------------------------------------------------
  Soln.name       Mo-std
  ----------
  Mass conc.        10 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: AB132               CALCULATION
                            max. 15 lines
-------------------------------------------------------------------------------

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

Fig. 1 Method for the Mo determination with the 746 VA Trace Analyzer

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 06021514             User:                      Date: 1999-06-02
 Modified    : 2000-11-29 19:45:24  Run :  0                   Time: 15:14:44
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
  1     sample                                                        10 mL
--------------------------------------------------------------------------------
 Method  :  AB132
 Title   :  Det. of Mo in strong samples cont. Fe. AB 132
 Remark1 :  10 mL sample cont. 0.25 mol/L HNO3 + 1.6 g NH4NO3
 Remark2 :
--------------------------------------------------------------------------------

  Substance : Mo                                                 Comments
  Mass conc.:    22.06 ug/L            Mass     : 220.6 ng      ------------------
  MC.dev.   :    0.112 ug/L (0.506%)   Add.mass :   200 ng
  Cal.dev.  :    -                     V0.sample:    10 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -179   -4.592  -4.590   0.0028
              01   -180   -4.588
              10   -179   -8.743  -8.737   0.0082   -4.147
              11   -179   -8.731
              20   -179   -12.84  -12.86   0.0348   -4.125
              21   -180   -12.89

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Mo           std.add.     -4.591e-09   -2.081e-04                 1.804e-11

C#  Workg.com.var  Remark
 --  -------------  ---------------

 Final results                        +/- Res.dev.   %      Comments
 ---------------------------------    -----------------    ------------------
         Mo =   22.062 ug/L              0.112   0.506
```

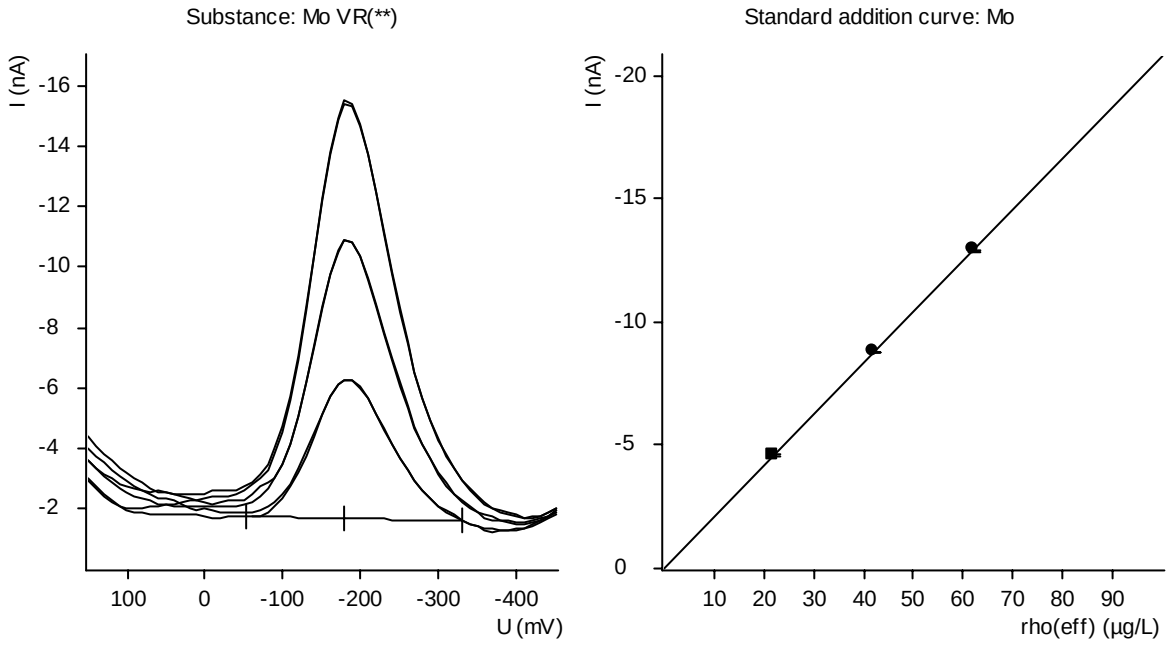

Fig. 2 Example of a Mo determination with the 746 VA Trace Analyzer