Application Bulletin

Metrohm

Of interest to:
General
Oil-refinery laboratories

No. 50/2 e

Polarographic determination of lead in petrochemical products

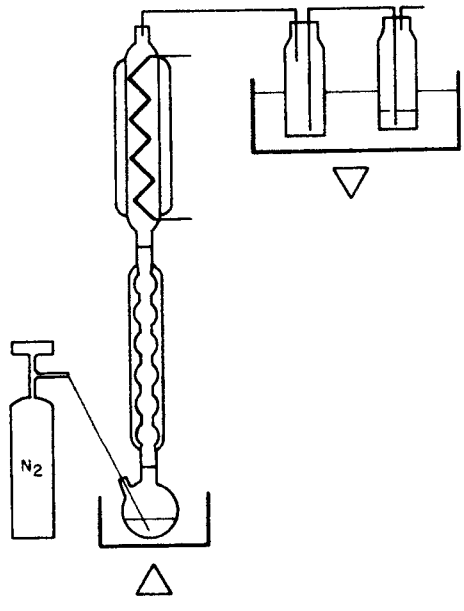
Summary

The determination of the lead content in engine fuels has gained considerable importance since the introduction of the catalyst technique. Even small contents of lead injure the effectiveness of the catalysts or may destroy them. On the other hand, there are still many vehicles on the market which are driven with leaded fuel (additions of tetraalkyl lead). Here also, the knowledge of the lead content is of interest.

With reference to DIN 51769 and ASTM D-1269 a simplified procedure for the determination of lead in petrochemical products is described. The products are disaggregated with HCl and the lead compounds are transferred in lead(II)chloride. After extraction with water, the inverse voltammetric Pb determination is carried out.

Apparatus

- 2.506.0010 Polarecord or 2.626.0010 Polarecord
  with 2.663.002X VA Stand and 2.608.0010 VA Controller
  or
  2.646.003X VA Processor with 2.647.0020 VA Stand
- Reflux apparatus



Reagents

- Hydrochloric acid: $w(HCl) = 0.36$ AR grade or "Suprapure" (36%)
- Heavy fuel: boiling range 200...240 °C
- Nitrogen: out of steel bottle with reducing valve
- Pb standard: $\rho(Pb) = 1$ g/L.
  1.599 g $Pb(NO_3)_2$ are diluted in AR grade water and mixed with 1 mL conc. nitric acid. Dilute to 1 L with AR grade water.
  By diluting with AR grade water standards with lower concentrations are prepared.
- AR grade water

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Sample preparation/ extraction

- The apparatus is constructed according to illustration on page 1. 10 mL heavy fuel, 10 mL HCl and 10 mL sample are pipetted into a round flask with two openings. Bubble N_2 through the mixture and boil for 45 min under reflux (with 15 min only 90% of the lead is extracted).
- After brief cooling draw-off the lower aqueous phase almost completely with a measuring pipette and put it into a 50 mL graduated flask. Add a further 10 mL AR grade water to a round-bottom flask and boil again for 5 min.
- After cooling transfer the mixture into a separating funnel, pour the aqueous extract also into a graduated flask, fill it with AR grade water to the mark and mix.

Method

Add 15 mL AR grade water into the the polarography vessel. According to the lead content use now different quantities of extraction solution and different enrichment periods:

lead content mg/L: 100 µL extraction solution

lead content µg/L: 5 mL extraction solution

The HCl of the extraction solution serves as base electrolyte. As it is also present in different quantities because of the different sample sizes, the peak potentials of the lead are displaced correspondingly.

	100 µL sample size	5 mL sample size
method/amplitude	DP / +30 mV	DP / +30 mV
U set	–0.7 V	–0.7 V
enrichment period	60 s	180 s
U stop	–0.2 V	–0.3 V
sweep rate	10 mV/s	10 mV/s
$E_{P(DP)}$ Pb	app. –0.27 V	app. –0.43 V

The determination of the content is carried out according to the standard addition method. A blank value (inclusively extraction step with heavy fuel, however without sample) has to be determined and to be deducted.

Remarks

- The determination limit conforms to the blank value, which, under observance of the above instructions, lies at 10...20 µg/L Pb approximately.
- The detection limit lies under 1 µg/L Pb.
- In order to keep the apparatus free of lead, it is rinsed with warm, diluted nitric acid (app. 10%). The polarographic measuring cell can be cleaned with cold nitric acid of the same concentration.

Literature

- DIN 51769 Part 1 and Part 4
- ASTM D-1269
- Roschig M., Matschinger H.
  Determination of Pb-traces in technical hydrocarbon mixtures by inverse-voltammetry.
  Chem. Technol. 19, (1967) 103–104
- Marti M.
  Determinazione polarografica del piombo in microquantita nei distillati leggeri.
  La Rivista dei Combustibili 15/6, (1971) 252–255
- Guinon J.L., Grima R.
  Influence of surfactants on the gasoline-water emulsion. Polarography of lead and the determination of lead in gasoline.
  Analyst 113, (1988) 613–615

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Example

Determination of lead in "red" fuel: Program of the 646 VA Processor

```
   Determination of lead in petrol                    METHOD 14  PAGE 3
   MPL 1          EL.TYPE MME                         OPERATION SEQUENCE

   OPERATIONS/PARAMETERS                 OPERATIONS/PARAMETERS
 1 STIR  ;PURGE ;        300  s      11a    U.END             -200  mV
 2 @PURGE;                           11b    U.STEP             4  mV
 3 [ADDL ;                                  SW.RATE           10.0 mV/ s
 4 @PURGE;                           12 @MEAS ;STIR  ;
 5 NOP   ;              10  s       13 REP) 1;
 6 (REP  ;              14 PURGE ;BEEP  ;
 7 HMDE  ;              15 ADD1[2;
 8 MEAS  ;              60  s       16 END   ;
 8a    M.MODE      DPN   30  mV
 8b    T.STEP            400  ms
 8c    U.SET            -700  mV
 9 @STIR ;
10 MEAS  ;              4  s
10a    M.MODE      DPN   30  mV
10b    T.STEP            400  ms
10c    U.SET            -400  mV
11 SWP 0 ;              20  s
```

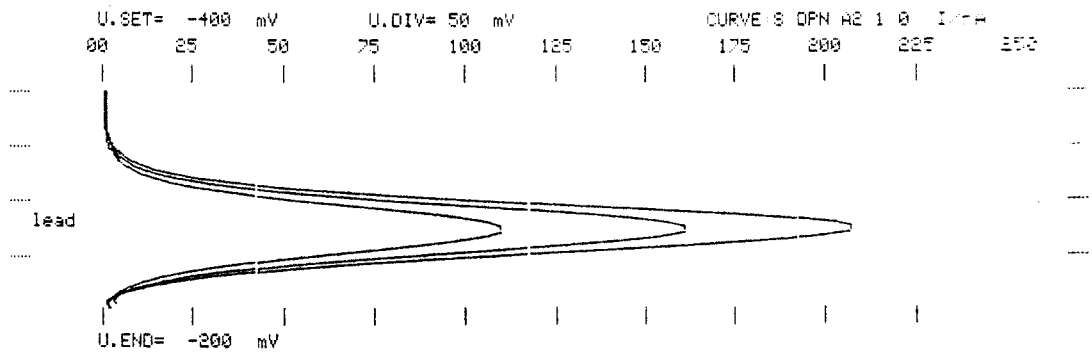
Determination of lead in "red" fuel: Resultat block of the 646 VA Processor

```
METROHM 646 VA-PROCESSOR  (5.646.5041)
Determination of lead in petrol                    METHOD  14
MPL  1         EL.TYPE   MME

SUPP.ELEC      HCl of digestion
V.MEAS          15.000 mL
ALIQUOT         2.000   E- 3

REMARK         digestion DIN 51769 : 10ml petrol + 10ml HCl p.a
                + 10ml sample
NAME           fra
RUN#            13

    ANALYTE    L R S       U.SUBST      EV.VALUE    DELTA        m.ANALYTE
    lead       A0 0 0      -274  mV      101.7 nA
               A0 1 0      -274  mV      105.5 nA
               A1 0 0      -274  mV      152.5 nA
               A1 1 0      -274  mV      155.6 nA    50.47 nA
               A2 0 0      -274  mV      200.4 nA
               A2 1 0      -274  mV      202.4 nA    47.32 nA
            m.STD    1.500 ug     SLOPE    30.67 ug/uA          2.999 ug

    rho (Pb)    =    149.9         mg/l

    SMPL.V/m          10.0000 mL          IDENT red petrol
    DATE  89-08-10  TIME   17:30
```

Polarographic determination of lead in petrochemical products

Example

Determination of lead in "red" fuel: Example of curve of the 646 VA Processor



Determination of lead in "red" fuel:
Program of the 646 VA Processor for the determination of the blank value in µg/L (or for "green" fuel)

```
Determination of lead in petrol                    METHOD 14  PAGE 3
MPL 1          EL.TYPE MME                         OPERATION SEQUENCE

   OPERATIONS/PARAMETERS                              OPERATIONS/PARAMETERS
 1 STIR  ;PURGE ;          300  s        11a   U.END              -200  mV
 2 @PURGE;                               11b   U.STEP              4  mV
 3 [ADDL ;                                     SW.RATE             10.0 mV/ s
 4 @PURGE;                               12  @MEAS ;STIR  ;
 5 NOP   ;                10  s         13  REP) 1;
 6 (REP  ;                               14  PURGE ;BEEP  ;
 7 HMDE  ;                               15  ADD1]2;
 8 MEAS  ;                180  s        16  END   ;
 8a    M.MODE      DPN     30  mV
 8b    T.STEP              400  ms
 8c    U.SET              -700  mV
 9 @STIR ;
10 MEAS  ;                4  s
10a    M.MODE      DPN     30  mV
10b    T.STEP              400  ms
10c    U.SET              -400  mV
11 SWP 0 ;                20  s
```

Determination of the blank value: Example of curve of the 646 VA Processor