Table 1. Effect of various parameters on the absorbance of the Re-thiocyanate complex

Temperature[a], °C	40	45	50	55	60	65	68	70	72	75	80	85
Absorbance	0.028	0.047	0.120	0.218	0.600	0.629	0.635	0.635	0.635	0.620	0.595	0.569
KSCN[b], ml	0.0	0.5	1.0	2.0	3.0	3.5	3.9	4.0	4.1	4.5	5.0	6.0
Absorbance	0.011	0.190	0.400	0.595	0.635	0.655	0.670	0.670	0.670	0.665	0.650	0.625
Ascorbic acid[c], mg	0.0	20	50	100	200	250	290	300	350	500		
Absorbance	0.530	0.590	0.615	0.640	0.665	0.668	0.670	0.670	0.670	0.670		
HCl[d], mol/l	0.0	0.2	0.3	0.8	1.0	1.5	1.9	2.0	2.1	2.5	3.0	
Absorbance	0.014	0.017	0.029	0.109	0.140	0.610	0.670	0.670	0.670	0.650	0.625	
Equilibration time[e], min	0.5	1.0	2.0	3.0	4.0	5.0						
Absorbance	0.658	0.670	0.670	0.670	0.670	0.669						

Conditions:
[a] Re = 100 µg; KSCN = 3 ml; Ascorbic acid = 300 mg; HCl = 2 mol/l; colour development time = 5−6 min; final aqueous volume = solvent volume = 20 ml; equilibration time = 1 min
[b] Temperature = 70°C, other conditions are the same as in (a) excepting KSCN
[c] KSCN = 4 ml, other conditions are the same as in (b) excepting ascorbic acid
[d] Ascorbic acid = 300 mg, other conditions are the same as in (c) excepting acid concentration
[e] HCl = 2 mol/l, other conditions are the same as in (d) excepting equilibration time

sorbances are measured at 400, 430, 450 nm. The three curves obtained by plotting mole fractions of rhenium against their respective absorbance values indicate two maxima corresponding to metal: ligand ratios of 1:4 and 2:3 in the extracted species. The mole ratio method [11] also confirms this inference.

Stability and sensitivity of the complex. The absorbance of the extract containing the Re-complex is stable for 2 h. Standard deviation is 0.002. Beer's law is obeyed in the range of 0 to 4 µg Re/ml. The molar absorptivity is 31162.79 l/mol/cm, Sandell's sensitivity is 0.0059 µg Re/cm^2.

References

1. Tribalat S (1949) Anal Chim Acta 3:113
2. Hurd LC, Babler BJ (1936) Ind Eng Chem Anal Ed 8:112
3. Hoffman JI, Lundell GEF (1939) J Res Natl Bur Standards 23:497
4. Sandell EB (1959) Colorimetric determination of traces of metals, 3rd edn. Interscience, New York, p 756
5. Geilmann W, Wrigge FW, Weibke F (1932) Z Anorg Chem 208:217
6. Geilmann W, Bode H (1948) Fresenius Z Anal Chem 128:489
7. Ryabchikov DI, Borisova LV (1963) Talanta 10:13
8. Koz'licka M, Wo'jtswicz M, Adamiec I (1970) Chem Anal (Warsaw) 15:247
9. Nayak AN, Manjappa S, Ramappa PG, Yathirajan HS (1981) Fresenius Z Anal Chem 309:396
10. Job P (1928) Ann Chim 9:113
11. Yoe JH, Jones HL (1944) Ind Engng Chem Anal Ed 16:111

Determination of zinc in lubricating oil by polarography of emulsified samples

J. García-Antón and R. Grima

Departamento Ingeniería Química y Nuclear,
E.T.S.I. Industriales, Universidad Politécnica de Valencia,
P.O. Box 22012, E-46071 Valencia, Spain

Summary. A new polarographic determination of zinc in lubricating oils is based on the formation of an oil/toluene-water emulsion and bubbling nitrogen through the emulsion. A well developed peak appears at −1440 mV. The precision is ±3% for a sample with 382 mg Zn/kg.

Correspondence to: J. García-Antón

Introduction

The zinc complexes of organodithiophosphoric acid or zinc organodithiocarbamates are used as zinc additives in the commercial formulations of lubricating oils. They combine antioxidant properties with an ability to inhibit corrosion and to function as antiwear agents [1] in motor oil applications. The activity of zinc additives in the protection of rubbing metal surfaces depends on the concentration of the additive in the lubricating oil [2].

The standard method IP 117/82 [3] for the determination of zinc in unused lubricating oil requires the prior ashing of the organic matter at 550°C and acid digestion of the residue, the re-solution of the zinc and later precipitacion as zinc oxinate. All these operations are very tedious and time consuming. The standard method ASTM D-1549 [4] also follows the same way for the sample destruction and re-solution of the zinc. In the ASTM method the zinc determination is carried out by means of polarography in ammonium chloride-ammonia medium.

An alternative method is polarographic technique using the formation of an oil-water emulsion. The technique consists of
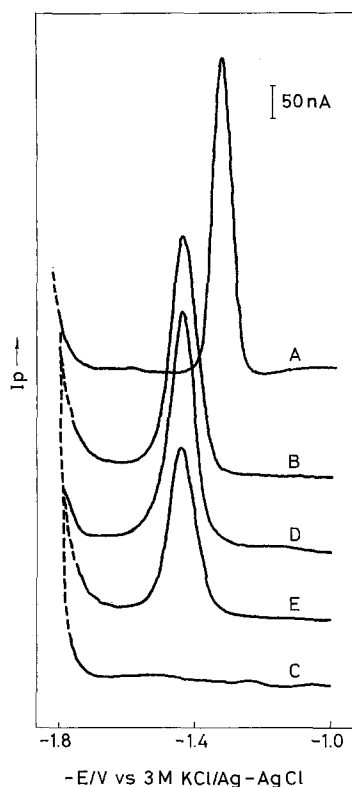
Fig. 1. Differential-pulse polarograms in ammonium chloride − ammonia medium. A 5 mg l^{-1} of aqueous zinc standard; B 5 mg l^{-1} of aqueous zinc standard with the addition of 1% Triton X-100; C 5 mg l^{-1} of aqueous zinc standard in lubricating oil/toluene − water emulsion; D polarogram C with bubbling nitrogen for 15 min; E 3.6 mg l^{-1} of zinc as hydraulic lubricating oil in emulsified medium

releasing the metal from an organometallic sample by means of an appropriate treatment (mineralization) and its transfer to an aqueous phase and subsequent emulsification. Aqueous standard solutions of the element to be determined are prepared and emulsified together with the same organic solvent in which the samples are dissolved. This technique has been used for the determination of cobalt (II) [5] and lead (II) [6] in paint driers and varnishes and for the determination of lead (II) [7] in gasoline. A new direct polarographic method for the routine analysis of zinc in lubricating oil industry is proposed.

Experimental

Apparatus and chemicals. Differential-pulse polarograms were obtained with a Metrohm E-505 polarograph and were recorded with a Metrohm E-626 Polarecord. The working electrode was a dropping-mercury electrode. The reference electrode was an Ag-AgCl with a 3 mol/l potassium chloride solution and the auxiliary electrode was a platinum wire. Nitrogen was bubbled through the solutions for 15 min. Zinc was used in the form of 100 mg/l Titrisol solutions (Merck). The surfactant used was Triton X-100 (Merck). Lubricating oils were obtained from Esso Española S.A. The other chemicals used were of analytical-reagent grade.

Procedure. Weigh accurately 10 − 15 g of the lubricating oil into a 50 ml calibrated flask and dilute to volume with toluene. Transfer 2 ml of this organic solution to a 50 ml calibrated flask. Add 1 ml of dilute chloric acid (1 + 1), shake gently for 10 min

Table 1. Determination of zinc in lubricating oil

Sample	Zn present ASTM mg kg^{-1}	Zn found DPP mg kg^{-1}	Difference mg kg^{-1}
ATF[a]	276	283	7
Hydraulic	382	407	25
Motor	1240	1202	−38

[a] Automatic transmission fluid
Mean values for three individually weighed samples

to release the zinc from the lubricating oil and emulsify with 5 ml of a 10% aqueous solution of Triton X-100. Add 5 ml of 1.3 mol/l ammonium chloride −7.5 mol/l ammonia buffer solution [8] and enough distilled water to bring the total volume to 50 ml.

The zinc content is determined by the construction of a calibration graph using an emulsified aqueous zinc(II) standard with an aqueous Titrisol solution of zinc(II). The organic phase consists of 2 ml of toluene solution of additive-free base lubricating oil. Repeat the process as for the above samples. The calibration graph is linear between 0 and 25 mg/l of Zn.

Results and discussion

The chloric acid addition allows to release zinc from the additive, transferring it to an aqueous phase as zinc(II). The polarographic peak of aqueous Zn(II) with the supporting electrolyte (ammonium chloride-ammonia) appears at very negative potentials, i.e. −1320 mV (Fig. 1A). The presence of Triton X-100, micellar solution, shifts the Zn(II) peak potential to more cathodic values (−1440 mV) and decreases the current by 27% (Fig. 1B). The lubricating oil/toluene-water emulsion shifts the Zn(II) peak potential to even more cathodic values, introducing the Zn(II) peak into the medium peak, (Fig. 1C). Bubbling nitrogen through the solutions draws the toluene off the emulsion and a well developed peak appears at −1440 mV with the same Ip C^{-1} relation as the Zn(II) peak in micellar solution (Fig. 1D). The emulsion behaves as micellar solution. The calibrated graph can be made with Zn(II) in micellar medium or in emulsion medium, bubbling nitrogen until reaching a constant peak current.

For all the lubricating oils analysed (Table 1), the difference between the proposed polarographic method and the ASTM D-1549 standard method was not greater than 6.5%. The precision, calculated from the relative standard deviation of five replicate determinations, was 3% for a sample containing 382 mg kg^{-1} of zinc.

References

1. Wang SS, Maheswari SP, Tung SC (1989) Tribol Trans 32:91
2. Plaza S (1987) ASLE Trans 30:241
3. IP 117/82. Standards for petroleum and its products, Part 1, Volume 1 (1985) Institute of Petroleum, London
4. ASTM Standard D-1549, Part 23 (1981) American Society for Testing and Materials, Philadelphia, p 817
5. García-Antón J, Guiñón JL (1985) Analyst 110:823
6. García-Antón J, Guiñón JL (1986) Analyst 111:1365
7. Guiñón JL, Grima R (1988) Analyst 113:613
8. Vogel's (1978) Texbook of quantitative inorganic analysis, 4 ed, Longman, London, p 321