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DETERMINATION OF TRACE LEVELS OF TITANIUM IN POLYOLEFIN POLYMERS BY CATALYTIC REDUCTION USING SQUARE WAVE VOLTAMMETRY*

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Summary—A sensitive and rapid method for the determination of trace levels of titanium in polyolefin polymers using square wave voltammetry is discussed. It involves ashing, acid digestion of polymer samples and determination of titanium(IV) by catalytic reduction using square wave voltammetric (SWV) technique. A well defined peak of titanium(IV) in Britton–Robinson buffer solution containing EDTA and $KBrO_3$ is observed in the potential range of −0.10 to −0.40 V *vs.* Ag/AgCl. Calibration graphs were linear in the range 0.05–0.25 μg/ml for titanium. Effects of pH and concentration of bromate, EDTA and buffer constituents are studied for the optimization of experimental conditions. Interference from other concomitants present in the polymer matrix are studied. Low density polyethylene (LDPE) obtained by tubular process was used for preparing the synthetic standards in order to optimize the experimental conditions and good recoveries (99–101%) were obtained. The method was extended to different polyolefin samples and the results obtained for the titanium content compared with those obtained by UV/Vis spectrophotometry. Statistical evaluation showed no significant bias between the two methods. SWV is found suitable for the estimation of Ti in the range 1–50 μg/g in polyolefin polymers with a RSD < 2.0%.

The origin of trace metals in polymers is mainly from two sources: elements which occur in deliberately added substances such as polymer additives or elements which occur as adventitious impurities like catalyst residues or process contaminants. Production catalyst residues at trace levels remaining in polyolefins can have a significant effect upon the life-time expected from this resin in telecommunication applications.[1] During the manufacture of polypropylene and ethylene-propylene copolymers using polymerization catalysts consisting of titanium halides and organo-aluminium compounds, the final polymer contains traces of aluminium, titanium and chloride.[2] For a variety of reasons, ranging from control during the manufacturing process to the identification of unknown material, it is necessary to be able to determine accurately the concentration of elements in these polymers.

The analysis of trace metals in polyolefins is often problematic, since it involves prior separation of these elements from the polymer matrix by ashing and dissolution using suitable chemical reagents followed by an appropriate analytical technique for quantification of trace metallic residues. These methods involve instrumental techniques, *e.g.* UV/Vis spectrophotometry,[2] X-ray fluorescence spectrometry (XRF),[3] atomic absorption spectrometry (AAS)[4] and neutron activation analysis (NAA).[5] However, voltammetric techniques are seldom used for such investigations even though the sensitivity limits are comparably quite high.[6] Due to difficulties in the atomization process, AAS is not a preferred technique for estimating trace amounts of titanium.[7] Titanium atomization is prone to severe matrix interferences and the sensitivity is very low (analytical range: 50–200 μg/ml). Inductively coupled plasma (ICP) method is one of the most sensitive, but ICP analysis is time-consuming and very expensive.[8] The proposed voltammetric method is free from such problems and offers good sensitivity for the determination of trace levels of titanium in polyolefins.

EXPERIMENTAL

Apparatus

A Princeton Applied Research (PAR) Model 384-B polarographic analyser system together

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*I.P.C.L. Communication No. 254.

with a PAR 303A static mercury drop electrode were used for all square-wave voltammetric measurements and the voltammograms were recorded on a Houston DMP-40 digital plotter. Potentiostatic control of the electrode potential was established by three electrode system consisting of a static mercury drop working electrode, a platinum wire counter electrode and an Ag/AgCl/KCl (satd) reference electrode. Square wave frequency of 100 Hz and voltage scan rate of 200 mV/sec were used. The SWVs were recorded at 10^5 nA, whereas the CVs were recorded at 10^3 nA current settings.

An IBM PS/2 computer system with Lotus 1-2-3 and Harvard graphics software was used for all plots and computations. All spectrophotometric measurements were made on a Varian Superscan model-3 UV/Vis spectrophotometer using matched 1.0 cm quartz cells.

Reagents

All reagents used were of analytical grade. Water purified by means of a Milli-Q system was used for preparing the solutions. Aldrich AAS standard solutions of titanium of 1000 μg/ml were used for preparing calibration standards. Stock solutions of 0.1*M* EDTA and 0.5*M* $KBrO_3$ were prepared by taking appropriate amounts of the respective salts.

Sample dissolution

Polymer sample (30 g) along with 3 g of breakdown mixture (1:3 mixture of KNO_3 and K_2SO_4) were weighed out into a platinum crucible and heated until the polymer began to decompose. The heating was controlled so that the combustion never became violent. The crucible was made red hot in order to eliminate carbonaceous residues. They were cooled and 4 ml of the reagent solution added (a mixture of 5% H_2SO_4 and K_2SO_4 solutions) slowly along the walls of the crucible. They were heated again to dryness and, after cooling, 2.5 ml of 12.5% H_2SO_4 added and the residue dissolved by gentle heating. The contents were quantitatively transferred into a 25 ml volumetric flask and made up to the mark with demineralized water.

Low density polyethylene (LDPE), processed in tubular reactors by gas phase polymerization in the absence of any catalyst, was used as matrix for preparing polymer standards. Titanium was incorporated to achieve a final concentration in the range of 2–20 μg/g, and the procedure described above followed for preparing synthetic solutions. Sample solutions thus prepared to contain final concentrations of 10, 5, 4 and 3 μg/g of titanium in the polymer matrix are designated as PE1, PE2, PE3 and PE4. In the case of other polymers such as polypropylene (PP), ethylene–propylene copolymer (PPCP), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE), the same dissolution procedure was adopted and the digests made up to 25 ml. In the case of LLDPE and HDPE, wherein the titanium content is comparatively high, a diluted stock solution was used for SWV experiments.

Procedure

Solution volume in the experimental cell was kept at 10 ml in which the concentration of titanium was varied from 0.05 to 0.25 μg/ml and the supporting electrolyte contained 1 m*M* EDTA, 5 m*M* $KBrO_3$ and 40 m*M* HBO_2 in Britton–Robinson buffer so as to adjust the pH to 2.5.

After 4 min deaeration, the square wave voltammograms were recorded from -0.1 to -0.4 V (*vs.* Ag/AgCl) and the height of the peak was measured at -0.26 V. Blank subtraction was applied for all the samples. Titanium content of each sample was determined by calibration procedure.

Titanium was estimated spectrophotometrically[9,10] in polymer digests using Tiron (*i.e.* disodium 1,2-dihydroxybenzene-3,5-disulphonate) as the colour developing reagent. The absorbance of the titanium(IV)–titro complex was measured at 390 nm.

RESULTS AND DISCUSSION

Mechanism of catalytic wave

The catalytic wave of titanium complexes has been studied by many investigators[11–14]. From these reports, the catalytic wave of the Ti(IV)–EDTA complex in the presence of bromate ion is an EC (heterogeneous electron transfer followed by homogeneous chemical reaction) mechanism:

$$Ti^{IV}Y + e^- \rightarrow Ti^{III}Y^- \quad pH < 2.5$$

$$6Ti^{III}Y^- + 6H^+ + BrO_3^- \rightarrow 6Ti^{IV}Y + Br^- + 3H_2O.$$

The mechanism of the process is rather complicated and the appearance of the maximum may be due to the relative change of the apparent rate constant of reoxidation caused by the effect of the double layer structure.[7] The catalytic wave thus produced is considered for quantifying trace levels of titanium in the present study.

Selection of experimental conditions

The compositions of supporting electrolyte can substantially change the reversibility and hence the magnitude of the square wave peak current. Reports with varied supporting electrolytes and complexing agents are available.[15,16] In the present study the combination of Britton–Robinson buffer as supporting electrolyte and EDTA as complexing agent gave the highest order of peak currents. Figure 1 shows the effect of supporting electrolyte concentration and pH on the peak current (i_p) of titanium system. Accordingly, optimum concentrations of EDTA, bromate and buffer constituents were chosen using 0.1 μg/ml of titanium in the synthetic solutions for obtaining maximum peak currents.

The square wave voltammograms of titanium(IV) at increasing concentrations (0.10–0.25 μg/ml) in the presence of polymer matrix and supporting electrolyte medium are shown in Fig. 2. The well-defined catalytic waves appear at -0.24 V (*vs.* Ag/AgCl). The analytical performance of the system is such that the calibration graph conformed to the equation $Y = 8.97X - 89.06$ [Y is peak current i_p(nA) and X is concentration c (μg/ml)] with a correlation coefficient of 0.998.

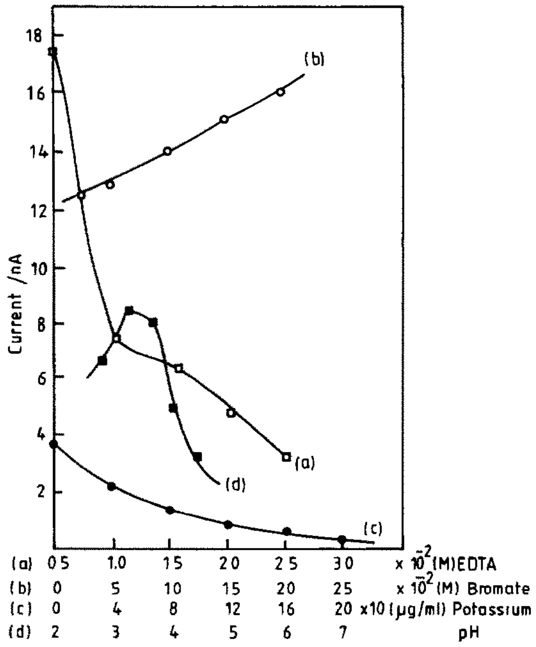

Fig. 1. Effect of supporting electrolyte concentration on peak height of Ti(IV) system.

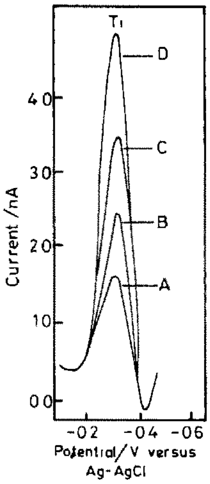

Fig. 2. Square-wave voltammograms of Ti in polymer digest with increasing analyte concentration: (A) 0.10; (B) 0.15; (C) 0.20; (D) 0.25 μg/ml.

Evaluation of laboratory-prepared samples

Since it was difficult to obtain titanium-free polypropylene samples, synthetic standards were prepared using tubular grade low density polyethylene (LDPE) which was produced under high pressure and in the absence of Ziegler–Natta catalysts. The effectiveness of the procedure was tested by analysing admixtures of titanium in polymers (PE_1–PE_4) such that composition was very close to that of commercial samples. These samples were brought into solution following the procedure described above. The samples were analysed by FAAS, UV/Vis and SWV methods. It has been found that the results obtained on FAAS are not satisfactory since the working range for titanium is 50–200 μg/ml (Analytical Data Manual, GBC 902 AAS). Another reason was that the catalyst concomitants as well as the ions from the breakdown mixture affect the atomization of titanium. Thus, FAAS is not a suitable method for determining very low levels of titanium in polyolefins. The results obtained from the SWV

Table 1. Results of recovery assays of titanium in the polymer samples

Sample No.	Metal added ($\mu g/g$)	Metal found ($\mu g/g$)*		% recovery	
		SWV	UV/Vis	SWV	UV/Vis
PE-1	10.00	9.96	9.89	99.60	98.90
PE-2	5.00	4.95	4.96	99.10	99.20
PE-3	4.00	3.98	4.10	99.50	102.50
PE-4	3.00	3.03	3.05	101.00	101.66
			MEAN:	99.80	100.56

*$n = 5$; RSD(SWV) < 2.0%; RSD(UV/Vis) < 2.0%.

Table 2. Determination of titanium (0.1 μg/ml) in the presence of foreign ions

Ion added	Metal to interferent ratio	% recovery
Barium	1:10	100.3
Magnesium	1:10	100.7
Calcium	1:1	98.9
Iron	1:1	75.3
Zinc	1:10	98.3
Vanadium	1:10	90.1
Aluminium	1:100	97.1

Table 3. Titanium contents of different polyolefins determined using SWV and UV/Vis methods

Sample No.	Titanium content (μg/g)	
	SWV	UV/Vis
POLY-1	4.95	4.91
POLY-2	4.79	4.84
POLY-3	3.94	4.08
POLY-4	3.83	3.93
POLY-5	14.70	14.58
POLY-6	45.50	45.00

method were compared with those of standard spectrophotometric method (Table 1). Recoveries of the order of 99–101% were obtained for titanium content by both the methods. The relative standard deviation was of the order of 2%, showing good reproducibility of the present method. UV/Vis spectrophotometry is also a suitable method for routine analysis. The only drawback is that relatively larger amounts (25–50 g) of polymer has to be processed for obtaining sufficient analyte concentration. In the present work, SWV is developed as an alternate method taking into consideration the quickness as well as sensitivity of this technique. For polymers containing 1–10 μg/g residual titanium, only 5 g of sample need be processed which is advantageous for routine analysis.

The possible interference of other elements present as coelements from catalyst residues and additives or impurities carried forward during the sample digestion process were studied by adding increasing amounts of interferent to a fixed concentration under optimal conditions after each addition. The results are summarized in Table 2. Interference from Fe and V were found to be high even at 1:1 molar ratio. However, the tolerance limits for other elements were good (analyte/interferent ratio >1:10). In the present study, most of the probable trace metal constituents of polyolefin polymers are found to be non-interfering.

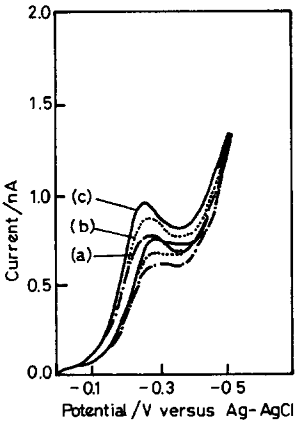

Fig. 3. Cyclic voltammograms for 0.1 μg/ml of Ti(IV) in the presence of 0.5 m*M* bromate 1 m*M* EDTA in B.R. buffer at different scan rates (a) 50; (b) 100; (c) 200 mv/s.

Cyclic voltammetry

The cyclic voltammetry of the system was investigated with a model 384-B polarographic analyser with a static mercury drop electrode. Figure 3 shows CVs for 0.1 μg/ml of titanium in the presence of 0.1 m*M* EDTA, 5 m*M* potassium bromate in 0.1*M* B.R. buffer obtained at different scan rates. A cathodic peak was observed at −0.26 V (*vs*. Ag/AgCl) during the scan in the negative direction. Reverse scan also produced a cathodic peak indicative of a catalytic process.[17]

Sample analysis

The acquisition of data for commercial polymer samples was carried out by following the same procedure as that used for laboratory prepared standards. A comparison of the results obtained for titanium contents of different polyolefins (POLY-1&2: polypropylene homopolymers; POLY-3&4: polypropylene copolymers; POLY-5&6: polyethylenes) by SWV and UV/Vis spectrophotometry is shown in Table 3. the results were subjected to *F*-test and at 95% confidence level showed no significant bias.

CONCLUSIONS

The results obtained here show that the proposed SWV method is fast, sensitive and better suited than conventional methods like AAS for the determination of titanium in polyolefin polymer samples. The reliability of the method is shown by the results of recovery studies and by the satisfactory determination in the commercial polymer samples. The procedure is simple and the effect of the reagents in SWV analysis is easily compensated by interactive matrix matching. The validity of the data obtained by SWV for Ti content in both standards and commercial samples has been verified with a complementary spectrophotometric method. LDPE samples have been successfully used as synthetic standards in the procedure. In conclusion, the potential of SWV in the determination of trace metals in polymers was explored and its versatility for both qualitative and quantitative analysis is demonstrated.

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REFERENCES

1. T. J. Elms and R. R. Pierson, *ICP Infn. Newslett.*, 1987, **13,** 41.
2. T. R. Crompton, *The Analysis of Plastics*, p.11. Pergamon Press, Oxford, 1984.
3. J. Haslam, H. A. Willis and D. C. M. Squirrell, *Identification and Analysis of Plastics*, p. 9. Butterworth, London, 1972.
4. D. Druckman, *Atom. Absorpt. Newslett.*, 1967, **6,** 115.
5. A. Krause, A. Lange and M. Ezrim, *Plastics Analysis Guide, Chemical and Instrumental Methods*, p. 220. Hanser Publishers, New York, 1983.
6. A. M. Bond, *Modern Polarographic Methods in Analytical Chemistry*. Marcel Dekker, New York, 1980.
7. Y. Yamamoto, K. Hasebe and T. Kambara, *Anal. Chem.*, 1983, **55,** 1942.
8. P. W. J. M. Boumans (ed.), *Inductively Coupled Plasma Emission Spectroscopy*, Part I, ch. 3. John Wiley & Sons, New York, 1987.
9. K. Oguma, S. Kozuka, K. Kitada and R. Kuroda, *Fres. J. Anal. Chem.*, 1991, **341,** 545.
10. G. S. Reddi, C. R. M. Rao, T. A. S. Rao and H. S. Muralidhar, *Anal. Chim. Acta*, 1991, **251,** 205.
11. P. J. Lingane and J. H. Christie, *J. Electroanal. Chem.*, 1967, **13,** 227.
12. H. Kaneko and T. Ozawa, *Bull. Chem. Soc. Jpn*, 1972, **45,** 140.
13. H. Kaneno and K. Kaneko, *Bunseki Kagaku*, 1979, **28,** 727.
14. V. F. Toropova and R. S. Zabbarova, *Zh. Anal. Khim.*, 1970, **25,** 1059.
15. R. L. Pecsok and E. F. Maverick, *J. Am. Chem. Soc.*, 1954, **76,** 358.
16. J. Osteryoung and K. Hasebe, *Rev. Polarog.*, 1976, **22,** 1.
17. J. Wang, J. Lu and Z. Taha, *Analyst*, 1992, **117,** 35.