Ion Chromatographic Determination of Phosphorus and Tungsten in Epoxidized Soybean Oil

Marino Quaglino, Nicola Bottazzini, Cecilia Querci, Marco Ricci* and **Silvano Cavalli**[1]
Istituto G. Donegani S.p.A., 28100 Novara, Italy

Soybean oil has been epoxidized with hydrogen peroxide in the presence of catalytic amounts of trioctylmethylammonium tetra(diperoxotungsto)phosphate. A fast ion-exchange chromatographic method with suppressed conductivity detection has been developed for determining residual contents of tungsten and phosphorus in the oil. Tungsten and phosphorus could be determined at concentrations of 66 and 11 ppm, respectively. At tungsten and phosphorus concentrations of 1000 and 50 ppm, measured repeatabilities were 1.3 and 1.5%, respectively.

KEY WORDS: Epoxidation, epoxidized soybean oil, soybean oil.

Epoxidized soybean oil is an important polyvinylchloride additive widely used to improve polymer flexibility and to assist in light and heat stabilization. Soybean oil usually is epoxidized with peroxyformic or peroxyacetic acids, but the reaction suffers from both safety and corrosion problems. Recently, a new catalytic method for the epoxidation of olefins with hydrogen peroxide under phase-transfer conditions has been reported (1-3). With soybean oil, using trioctylmethylammonium tetra(diperoxotungsto)phosphate (3) as catalyst (0.07 mol%, based on unsaturation) and a slight excess of diluted (33%) hydrogen peroxide, a clear yellowish oil has been obtained after 7 h at 60°C. The epoxidized soybean oil had low viscosity ($4.1–4.2 \cdot 10^{-4}$ m^2/s at room temperature), low residual unsaturation (iodine value = 2.7, corresponding to 98% double bond conversion) and high oxirane oxygen content (7.0%, corresponding to a 90% epoxidation selectivity). Similar results were obtained with more concentrated (70%) or more dilute (16%) hydrogen peroxide. The epoxidation resulted in a highly exothermic reaction with $\Delta H = -58$ to -62 Kcal/mol: the variability was probably due to the occurrence of side reactions (*e.g.*, oxirane hydrolysis), the extent of which depended on the chosen conditions. Gradual hydrogen peroxide feeding enabled control of heat evolution over the entire temperature range explored (40–70°C) up to a 5 kg scale.

Because a possible end use of epoxidized soybean oil is as an additive in polyvinylchloride food-wrap films, the need arose for determining residual tungsten and phosphorus contents in the oil. Usually, tungsten and phosphorus are determined by gravimetric (4) or spectrophotometric (5) methods, which require gram amounts of sample, element separation by selective precipitation and separate determination; these operations are both care- and time-intensive. The introduction and widespread diffusion of chromatographic techniques for inorganic compounds, particularly ion chromatography (6,7), which offers the possibility of determining more parameters in the same analysis without interference from the matrix and requires only small samples, prompted us to evaluate this technique for determining tungsten as tungstate ion (WO_4^{2-}) and phosphorus as phosphate ion (PO_4^{3-}). The chromatographic separation of these two anions (8) recently has been optimized by using a membrane suppressor (9), which can suppress more concentrated eluants, thus allowing the elution of strongly retained anions, *e.g.*, WO_4^{2-}, with anion exchange columns of moderate capacity, such as IonPac AS5 (Dionex Co., Sunnyvale, CA). Using this kind of instrumentation, the analysis can be completed within 10 min.

EXPERIMENTAL PROCEDURES

Instrumentation and reagents. An ion chromatograph 4000i (Dionex Co.) with suppressed conductivity detection was used. Data reduction and instrumentation control were both performed with an AI-450 chromatographic work station (Dionex Co.). Separations were carried out on an anion exchange column IonPac AG5 and a precolumn IonPac AS5 (Dionex Co.). An anion micromembrane suppressor AMMS (Dionex Co.) was used. All solutions were prepared with deionized water with conductivity <0.1 μS (MilliQ, Millipore Co., Milford, MA). Sodium hydroxide, anhydrous sodium carbonate, sulfuric acid, decahydrate sodium phosphate (Merck, Darmstadt, Germany) and dihydrate sodium tungstate (Novachimica, Milano, Italy) were reagent-grade. Soybean oil (Italiana Oli e Risi, Ravenna, Italy; iodine value 136) was found to be both tungsten- and phosphorus-free. The catalyst was analyzed before use, and tungsten and phosphorus contents were in accordance with the calculated values. Quartz crucibles (12 cm^3) were used for sample preparation.

Eluant and regenerant. The eluant was a 10 mM NaOH and 5 mM Na_2CO_3 solution. CO_2-free water and a moderate helium pressure were used in the eluant preparation. H_2SO_4 (25 mM) was used as the regenerant.

Calibration standards preparation. Four standard solutions were prepared for each element by diluting concentrated aqueous reference solutions (1000 mg/L of W and P, respectively) to final concentrations of 4, 10, 20 and 40 mg/L for tungsten and 0.4, 2, 3.4 and 5 mg/L for phosphorus. The solutions were transferred into quartz crucibles containing 100 mg of soybean oil and 0.5 mL of 1 M NaOH. The crucibles were heated to dryness at 150°C, carefully calcined with a Bunsen burner (caution: operate under hood), put in a pre-heated (250°C) muffle oven with air flow (50–60 mL/min), heated (25°C/min) to 750°C, maintained at this temperature for 45 min, and then cooled to room temperature. Deionized water (5 mL) was added, and the resulting solutions were magnetically stirred for 5 min.

Sample preparation. Soybean oil (50–100 mg) was weighed exactly in a quartz crucible and treated according to the above procedure, without adding tungsten or phosphorus.

Chromatographic conditions. The analyses were performed isocratically, with eluant and regenerant flows of

---

*To whom correspondence should be addressed at Istituto G. Donegani S.p.A., via Fauser 4, 28100 Novara, Italy.

[1] Present address: Dionex s.r.l., 20155 Milano, Italy.

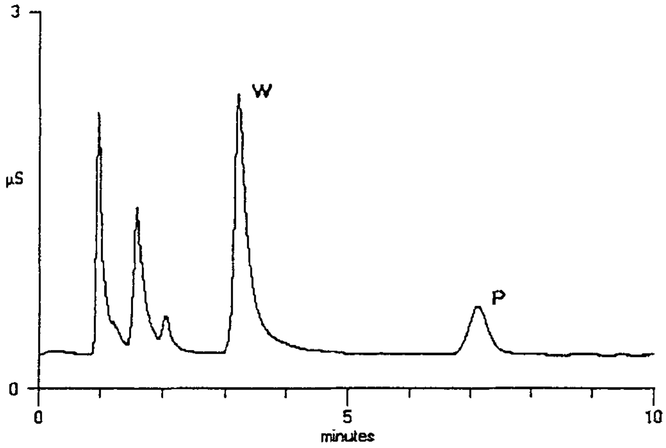

FIG. 1. Chromatogram of mineralized tungstate and phosphate ions from epoxidized soybean oil.

2 and 8 mL/min, respectively. The injection volume was 50 µL. A typical chromatogram of an epoxidized soybean oil sample is shown in Figure 1.

RESULTS AND DISCUSSION

Calibration curves. Calibration curves simply obtained by injecting standard solutions proved to be unsatisfactory; the resulting tungsten and phosphorus contents in reference soybean oil spiked with known amounts of the epoxidation catalyst were lower than expected (−3% for tungsten, −5% for phosphorus). So calibration curves were obtained after treating standards as the samples. Data used for tungsten and phosphorus calibration curves are shown in Table 1: good linearity is observed within the considered concentration range.

Soybean oil samples preparation. A careful study on sample preparation procedures was necessary to obtain reproducible and accurate results. The traditional nitric/sulfuric acid digestion required long preparation times, and adding two highly concentrated anions to the sample could introduce interference in the chromatographic analyses. Similar problems were encountered with microwave digestion, which required an acidic oxidant medium, *e.g.*, nitric acid. Therefore, controlled calcination with aqueous sodium hydroxide appeared to be the method of choice. This procedure offered several advantages: sodium hydroxide acted as a melting agent, converting both tungsten and phosphorus into soluble salts; the resulting solution was alkaline (like the chromatographic eluant); and it could be mixed fairly easily with oil samples. Some difficulties have been encountered in the choice of crucible. Noble metals (platinum, silver, gold) were rejected *a priori*, and other common metals (nickel and iron) were reactive (to some extent) toward hydroxyl ions and formed hydroxides, which could adsorb significant amounts of analytes. Porcelain and quartz also reacted with hydroxyls but to a lower extent. Best recoveries were observed with quartz, probably for two reasons: (i) quartz crucibles are less porous and more resistant to chemical attack, so the analytes' loss because of wall adsorption was negligible; and (ii) upon alkaline attack of quartz, sodium silicate was formed, which is completely soluble, whereas porcelain afforded insoluble hydroxides, which could adsorb or react with the analytes. Sample amounts of oil (50–100 mg) were chosen to obtain both good analytical sensitivities and short preparation times. Increased sample amounts significantly extended these times and were found to be preferred only when high sensitivity is desired.

Results. Tungsten and phosphorus contents in a typical sample of epoxidized soybean oil are reported in Table 2.

TABLE 1

Calibration Curves for Tungsten (W) and Phosphorus (P)

W (mg/L)	Peak area WO_4^{2-}	P (mg/L)	Peak area PO_4^{3-}
4	7830	0.4	4920
10	19871	2.0	25040
20	40622	3.4	44761
40	78188	5.0	63674
	r = 0.9997		r = 0.9995

TABLE 2

Tungsten (W) and Phosphorus (P) Values Found in Epoxidized Soybean Oil (ESBO)

Sample	W (mg/kg)	P (mg/kg)
ESBO/1	1440	67
	1400	63
ESBO/2	820	37
	840	35
ESBO/3	103	41
	98	45

TABLE 3

Recovery of Tungsten (W) and Phosphorus (P) Added to Soybean Oil as Liposoluble Epoxidation Catalyst

	W (mg/kg)					P (mg/kg)				
	Test 1	Test 2	Test 3	Average	Added amount	Test 1	Test 2	Test 3	Average	Added amount
ST44/89	381	405	407	398	406	20.4	20.4	19.1	20.0	19.3
ST45/89	996	981	960	979	1006	55.3	56.3	54.9	55.5	54.5
ST46/89	1736	1763	1752	1750	1780	72.8	72.6	74.1	73.2	72.6
Standard deviation			15.5					0.76		
RSD%[a]			1.5					1.5		

[a] Relative standard deviation (RSD)% value calculated on average concentration values of tungsten and phosphorus found in analyzed samples.

To verify the method's accuracy and repeatability, samples of soybean oil spiked with known amounts of both tungsten and phosphorus (as the liposoluble epoxidation catalyst) also were analyzed. As can be seen in Table 3, good repeatability was achieved ($RSD_W = 1.3\%$; $RSD_P = 1.5\%$); RSD = relative standard deviation.

The detection limits can be obtained from Table 1 data by using the equation $C_L = 3$ s/b, where C_L is the sample (5 mL) concentration in mg/L, s is the standard deviation and b is the slope of the calibration curve (10). Assuming a sample weight of 100 mg, detection limits were 66 and 11 mg/kg of oil for tungsten and phosphorus, respectively.

The ion chromatographic determination of tungstate and phosphate after epoxidized soybean oil mineralization is a fast and sensitive method to determine tungsten and phosphorus, if present, as contaminants derived from the epoxidation catalyst.

ACKNOWLEDGMENTS

This work has been sponsored by the Ministero dell' Università e della Ricerca Scientifica e Tecnologica within the framework of the "Programma Nazionale di Ricerca per la Chimica."

REFERENCES

1. Venturello, C., E. Alneri and M. Ricci, *J. Org. Chem. 48*:3831 (1983).
2. Venturello, C., R. D'Aloisio, J.C.J. Bart and M. Ricci, *J. Mol. Catal. 32*:107 (1985).
3. Venturello, C., and R. D'Aloisio, *J. Org. Chem. 53*:1553 (1988).
4. Erdey, L., in *International Series of Monographs on Analytical Chemistry: Volume 7, Gravimetric Analysis, Part II,* Pergamon Press, Oxford, 1954, p. 550.
5. Marczenco, Z., *Separation and Spectrophotometric Determination of Elements,* Ellis Horwood Limited, Chichester, 1986, Chapter 39.
6. Small, H., T.S. Stevens and W.C. Bauman, *Anal. Chem. 47*:1801 (1975).
7. Small, H., *Ion Chromatography,* Plenum Press, New York, 1989.
8. Zolotov, Y., O.Z. Shpigun and L.A. Bubchikova, *Fresenius Z. Anal. Chem. 316*:8 (1983).
9. Stillian, J., *L.C. Mag. 3a*:802 (1985).
10. Miller, J.C., and J.N. Miller, *Statistics for Analytical Chemistry,* John Wiley & Sons, New York, 1984, pp. 96–100.

[Received April 28, 1992; accepted September 16, 1992]