Technical

Analysis of Hydroformylated Vegetable Oils and Their Methyl Esters for Rhodium

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ABSTRACT AND SUMMARY

Two procedures for the determination of fat-solubilized rhodium were investigated. Analysis in aqueous media involves a sulfuric acid digestion which previously was carried out in 20-30 hr. Digestion now takes only 1 to 2 hr. The acid concentration in samples and standards is very critical. For analysis in nonaqueous media the sample is weighed, dissolved in methyl isobutyl ketone containing hydrogen chloride, and analyzed directly by atomic absorption spectrophotometry. Absorbance in both procedures follows Beer's law. Results varied when hydrogen chloride was omitted or replaced with phosphoric acid. The results agreed closely with results obtained by published colorimetric procedures.

INTRODUCTION

The selective hydroformylation (oxo rection) of fatty esters and glycerides using a rhodium catalyst supported on carbon or alumina has been described (1-3). Recently, a process for the recovery, reactivation, and reuse of the expensive rhodium catalyst used in preparing methyl formyl and carboxystearate (MFS and MCS) was reported (4,5). Determination of rhodium on commercial carbon and alumina supports and on spent supports by atomic absorption (AA) methodology has been described (6).

The actual determination by AA is rapid and the final results are comparable to standard colorimetric methods (7). However, these procedures when applied to fat (oxo products) solubilized rhodium require both a time consuming and tedious digestion. Sulfuric acid digestion of organic samples as small as 0.1 g normally are completed in 10 to 30 hr.

Sulfuric acid digestion of small samples (0.1 to 0.3 g) of fatty esters and glycerides containing 200-300 μg Rh/g using the published procedures (6) involved an initial charring after which the samples foamed excessively. These samples had low absorbance resulting in large errors in precision and accuracy. Digestion of 1-g samples to increase the amount of absorbance was difficult. This present study reports a rapid 1 hr sulfuric acid digestion of larger samples and the necessary AA methodology for determining fat-solubilized rhodium. Comparable results with a method where the fat is dissolved in methyl isobutyl ketone (MIBK) and analyzed directly by AA are also reported.

EXPERIMENTAL PROCEDURES

Methyl formylstearate and methyl carboxystearate were prepared as previously described (4,5).

Atomic Absorption Parameters

Samples for determination of rhodium were analyzed with a Perkin Elmer atomic absorption spectrophotometer Model 303 equipped with a readout recorder capable of expanding the scale 100X. Rhodium absorption was determined at 343.5 nm with a spectral band width of 0.235 nm and a lamp current of 30 ma. Analysis of wet-ashed samples containing sulfuric acid was made in a nitrous oxide-acetylene flame using a 5-cm single slot head. Nitrous oxide and acetylene rotometer settings were 6 and 12 units (13 and 6 liters/min), respectively.

Direct rhodium analysis of fat samples (100 mg) (no acid digestion) dissolved in MIBK was made in a fuel-lean air-acetylene flame using a 10 cm, 3-slot Boling burner head. The air and acetylene rotometer settings were 10 and 2 units (26 and 0.7 liter/min), respectively.

Preparation of Rhodium Standards

For wet-ashed samples, an aqueous stock solution of rhodium trichloride trihydrate (0.12789 g) (Alfa Inorganics, Beverly, MA) in a 100-ml volumetric flask was prepared. This solution when analyzed by colorimetric procedures (8) contained 500.2 μg Rh/ml. This solution was diluted to prepare a working stock solution containing 50 μg Rh/ml. Sulfuric acid (5 ml/25 ml, 20% by volume) was added to 2, 4, 5, and 8 ml aliquots and diluted to 25 ml. The acid was added to equal the acid concentration of the digested fat samples (6). The standard solution gave the straight line curve shown in Figure 1, curve E. Standards containing 1 to 4 ml sulfuric acid/25 ml are also shown (curves A-D).

Direct Determination in MIBK

Chlorotris(triphenylphosphine) rhodium (I) (Strem Chemical Inc., 150 Andover St., Danvers, MA) (0.300 g) was dissolved in MIBK and filtered to remove insolubles and diluted to 50 ml with MIBK. Three 1-ml aliquots were digested with conc. sulfuric acid (5 ml) and analyzed by comparison to the standard acid curve (Fig. 1, curve E). A working stock solution containing 75 μg Rh/ml MIBK was then prepared. Samples (4 ml) were again analyzed by the rapid sulfuric acid digestion procedure.

Eight standard solutions containing 0.15 to 2.1 μg Rh/ml were prepared in MIBK. Absorbance was obtained by direct aspiration of the standard solutions into a fuel lean air-acetylene flame. The standard curve is shown in Figure 2, curve A. Standard solutions containing distilled MFS (2, 4, 8 mg/ml) were also prepared. The curves for these three series of standards were almost identical and are shown as one curve in Figure 2, curve B. Curves for similar standards containing hydrogen chloride and phosphoric acid are shown in Figures 2 and 3.

For standards and samples containing hydrogen chloride or phosphoric acid, 5 ml of the acid stock solution was added before dilution to 25 ml. The two acid stock solutions were prepared by dissolving 35 g gaseous HCl in 160 g of cold MIBK and 50 ml of phosphoric acid in 150 ml of MIBK.

Determination of Fat Solubilized Rhodium

A. *Wet ashing with sulfuric acid:* MFS (100-300 mg) was weighed into a 30-ml Kjeldahl flask. Sulfuric acid (5 ml) and three glass beads were added. The flask was heated slowly and carefully until the initial charring and excessive

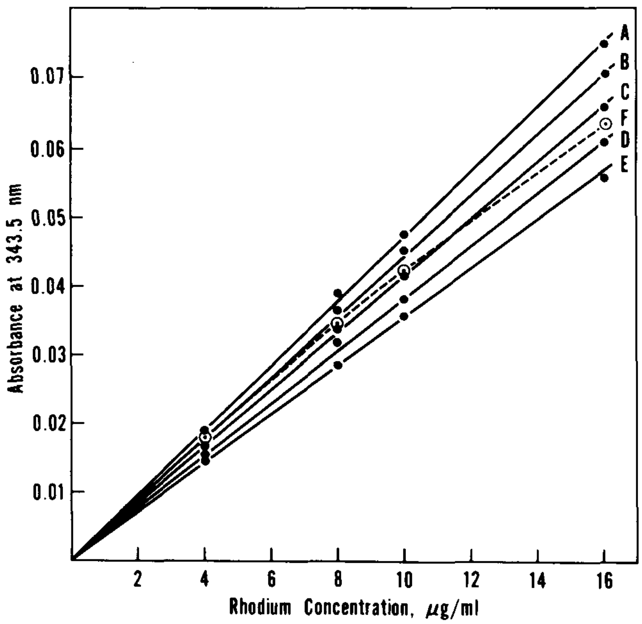

FIG. 1. Effect of sulfuric acid on the atomic absorption of rhodium. Rhodium standards with sulfuric acid (v/v): A, 4%; B, 8%; C, 12%; D, 16%; E, 20%; and F, no acid.

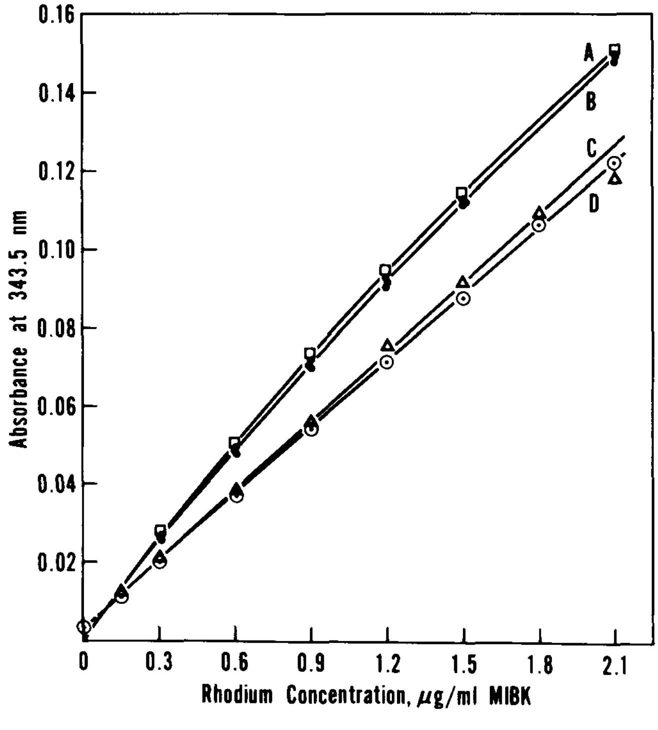

FIG. 2. Effect of HCl and methyl formylstearate (MFS) on the atomic absorption of rhodium. Curve A, Rhodium standards in methyl isobutyl ketone; Curve B, Standard contains 2, 4, 8 mg MFS/ml; Curve C, Rhodium standard contains 0.9 g hydrogen chloride; Curve D, Standard contains 0.9 g hydrogen chloride/25 ml solution and 4 mg MFS/ml.

foaming subsided. The solution was refluxed strongly enough to wash the sides of the flask and then refluxed until the solution became water white. Some samples required 10 hr but most required 20-30 hr for digestion. After cooling to room temperature, the contents were weighed and then transferred quantitatively (with caution) to a 25 ml volumetric flask. Additional make-up sulfuric acid to equal the weight of 5 ml of sulfuric acid in the standards was added. The samples were then diluted to 25 ml. The digested samples were analyzed by AA.

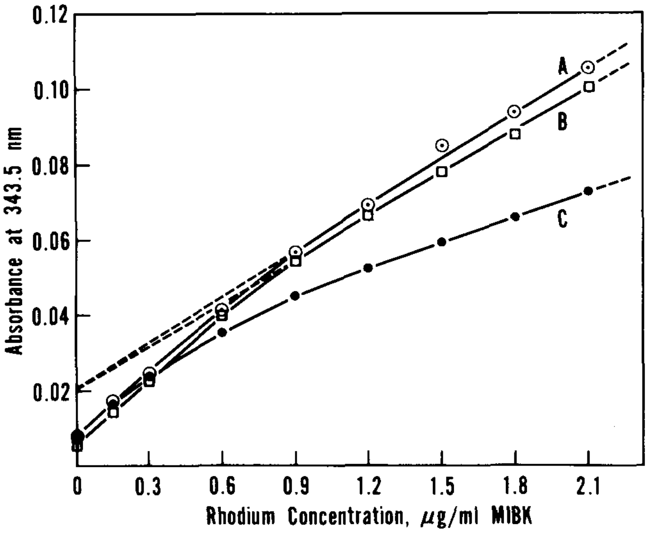

FIG 3. Effect of H_3PO_4 and methyl formylstearate (MFS) on the atomic absorption of rhodium. Curve A, Rhodium standards with 1 ml H_3PO_4/25 ml solution and 4 mg MFS/ml; Curve B, Standards with 1.5 ml H_3PO_4/25 ml solution and 4 mg MFS/ml; Curve C, Standard with 1.5 ml H_3PO_4/25 ml solution.

B. *Distillation followed by wet ashing:* One-gram oil samples containing more than 100 μg Rh/g oil or 5-g oil samples containing less than 100 μg Rh/g oil were weighed into a 30-ml Kjeldahl flask. The sides of the flask were washed with solvent and the flask was heated to reflux (fume hood). The vapors were ignited and the oil was distilled to dryness. The residue was then digested with 5 ml of sulfuric acid as described above (long digestion procedure 10-30 hr).

C. *Distillation, volatilization of carbon residues and wet ashing:* A rapid 1 hr digestion of the residue was usually carried out by adding sulfuric acid (1 ml) and refluxing to wash the sides of the flask and to obtain a homogeneous solution. After a few minutes the acid was distilled to dryness (fume hood) and the sulfated residue heated strongly (but not to red-glass stage) to a point where the carbonaceous residue appeared to volatilize, leaving an almost clean flask. Occasionally a sample required a second 1 ml acid treatment. After cooling, sulfuric acid (5 ml) was added, refluxed for 1 hr, weighed, diluted as described above, and analyzed by AA using aqueous acid standards. The total time to weigh and digest the sample was usually 1.5 hr.

D. *Direct determination in MIBK:* The hydroformylated fatty ester or oil (100 mg) was weighed into a 25-ml volumetric flask. Hydrogen chloride or phosphoric acid in MIBK if used in standards was added before dilution to volume with MIBK. Rhodium was determined by AA by direct aspiration of the solution and the μg Rh/ g oil was obtained directly from a standard curve of absorbance vs rhodium concentration (Figs. 2 and 3).

RESULTS AND DISCUSSION

In this work, AA analysis of fat-solubilized rhodium was carried out in both aqueous and organic media. In aqueous media the sample was first digested with sulfuric acid followed by aspiration into a nitrous oxide-acetylene flame. In organic media, the fatty sample was dissolved in MIBK and analyzed by direct aspiration of the solution into a fuel-lean, air-acetylene flame. Analytical results obtained by methods A-D are summarized in Table I.

Wet Ashing with Sulfuric Acid

The results of analysis by AA procedures for rhodium on

TABLE I

Comparison of Methods for Determination of Rhodium in Oxo Products

		H_2SO_4 digest[a]				MIBK[b]				
		Slow			Rapid[c]			HCL	H_3PO_4	
Sample	Colorimetric (7,8) (µg/g)	Wt (g)	Time (hr)	(µg/g)	(µg/g)	-MFS (µg/g)	+MFS[d] (µg/g)	+MFS[d] (µg/g)	-MFS (µg/g)	+MFS[d] (µg/g)
MFS[b,e]	202	0.1	24	233	180	161	181	176	208	212
	185	0.1	26	206	176	165	180	181	208	210
	182	0.3	22	184	186	168	184		208	211
		0.3	29	187	186					
					183					
					186					
MFS[b,f]	271	0.1	18	293	274	235	262	267	282	285
	276	0.1	19	293	275	235	264	267	284	286
	261	0.3	22	293	275	237	266	260	283	288
		0.3	23	275						
MFS[b,f,g]	296				276	236	282	274	284	276
	288				283	235	282	272	284	282
	279				279	237	285	246	285	288
MFS[f]	280	0.1	20	333	274	322	327	291	314	309
	273	0.1	19	286	281	322	327	282	317	308
	276	0.3	23	295	280	329	327	293	315	308
					285	329				
					286					
					282					
	—			—	—	—	—	—	—	—
Standard deviation	8.05			19.4	5.8	2.95	1.68	9.27	0.96	3.15
Relative standard deviation	3.1			7.4	1.5	1.2	0.6	3.6	0.4	1.2

[a] Standards and samples contained 5 ml sulfuric acid/25 ml solution.

[b] MIBK = methyl isobutyl ketone, MFS = methyl formylstearate, MCS = methyl carboxystearate (5).

[c] One-gram sample; distilled, dissolved in acid, carbon residue volatilized, and then digested 1 hr.

[d] Standards contained 100 mg pure MFS.

[e] Prepared with 5% Rh on alumina.

[f] Prepared with freshly calcined 5% Rh on alumina (4)

[g] Sample 2 yr old.

commercial carbon and aluminum supports digested with sulfuric acid are comparable to analysis by established colorimetric procedures (7,8), which in addition to the acid digestion also requires a stannous ion reduction.

Potassium bisulfate (9) and sulfuric acid (6) have been reported to enhance the absorbance. However, as the acid concentration is increased from 4 to 20% by volume (Fig. 1, curves A-E) the absorbance decreases. Thus, the digested samples were weighed and sulfuric acid was added to match the exact weight of 5 ml of sulfuric acid in the aqueous rhodium trichloride standards (Curve E). For a given acid concentration, absorbance vs rhodium concentration follows Beer's law and was reproducible over a period of several months. As shown in Figure 1, curve F, aqueous rhodium trichloride standards without acid did not obey Beer's law. The enhancement of rhodium absorption at low sulfuric acid concentration (4%) can probably be attributed to a releasing effect (10) where sulfuric acid prevents the formation of metallic clotlets in the flame, and as the solution evaporates the rhodium is released in atomic form. At higher concentration (above 8%) decreased absorption is probably a matrix effect in which increased viscosity and surface tension restrict the flow of solution into the premix atomizer chamber (11).

Flame temperature is a critical parameter when determining rhodium by atomic absorption. Heneage (12) has shown that in air-acetylene flames rhodium absorption is markedly affected by the fuel to air ratio. Fuel-lean oxidizing flames are recommended for rhodium determinations. Further, in the first few minutes of analysis of rhodium using air or nitrous oxide-acetylene flame, absorbance of the Rh solution has a tendency to increase slightly with time. Thus aspiration of water or MIBK into the flame for 15 min to allow the burner head to stabilize is also recommended.

After the foaming subsided, refluxing was continued until the solution was water white. For some samples this was accomplished in about 10 hr but most required over 20 hr. This lengthy digestion procedure was eliminated by using a rapid digestion method whereby samples up to 5 g weighed into a Kjeldahl flask were first distilled to dryness, refluxed with sulfuric acid (sulfated), and then heated strongly (but not to the red-glass stage) to a point where the sulfated carbonaceous residue disappeared. The sample was then refluxed 1 hr with sulfuric acid. Even the commercial catalyst on carbon was readily and rapidly digested by this procedure. The time of digestion and analysis are shown in Table I. Samples that were distilled to dryness, the carbon residue (no sulfuric acid treatment) heated to red-glass stage, and then dissolved in sulfuric acid were always about 10% low in rhodium when compared to samples that were first sulfated. Apparently some rhodium fuses to the glass or is reduced to metallic Rh, thus becoming more difficult to dissolve or digest with acid. Physical removal of rhodium with the fumes (at first water vapor, then soot) is also possible, which apparently does not happen in samples pretreated with sulfuric acid.

Total Rhodium Balance

A rhodium balance for one hydroformylation reaction was carried out using the 1 hr digestion procedure. Rhodium on carbon (5%, Engelhard Industries, Newark, NJ) is slightly hydroscopic and when analyzed (three determinations by AA, 2 hr sulfuric acid digestion) contained 4.95% Rh. Hydroformylation of methyl oleate (75 g) with 0.750 g of catalyst (contained 37.13 mg Rh) and triphenylphosphite (0.750 g) yielded 85.0 g of MFS containing 283.1 μg Rh/g (total 23.78 mg Rh). The spent catalyst contained 12.52 mg Rh. Thus, the 36.30 mg of the total 37.13 mg Rh accounts for 97.8% of Rh used for the reaction.

The rapid digestion procedure (distillation, predigestion with acid, volatilization of the carbon residue, and acid digestion) gave similar results when applied to hydroformylated soybean methyl esters and glycerides. From the results the rapid digestion procedures (1 hr), where sulfuric acid to replace that volatilized during digestion is added to equal the exact weight of acid used in the standards, is recommended over the conventional digestion procedure previously reported (6). This procedure can possibly be used to determine other fat-solubilized metals except nickel where volatile nickel carbonyl would be formed.

Direct Analysis in MIBK

Direct aspiration of MIBK-fat solutions into the AA flame has found widespread use as a rapid and conventional method for determination of trace metals in vegetable oils (13-15). Diely (16) reported a method for AA determination of rhodium in mixtures of organic solvents. This appears to be the only analytical method of determining rhodium in organic solvents reported in the literature. The excellent sensitivity of rhodium to AA coupled with a high signal-to-noise ratio (12) and the relatively high rhodium content of oxo products are ideal factors favoring development of a scale expansion method for rhodium.

Standard solutions in MIBK containing 0 to 2.1 μg Rh/ml for analysis by direct aspiration into the AA flame were prepared from chlorotris(triphenylphosphine) rhodium (I). The standard curve shown in Figure 2, curve A, however, does not obey Beer's law. Absorbance is not linear with increasing rhodium concentration. Standards containing 2, 4, and 8 mg MFS/ml (curve B) had a slight decrease in absorbance but still were not linear. Absorption of standard solutions containing phosphoric acid (1 and 1.5 ml/25 ml solution) as the releasing agent and distilled MFS (4 mg/ml) to match the matrix effect was enhanced (Fig. 3, curves A and B) when compared to absorption of standards containing only phosphoric acid (curve C). Standards with phosphoric acid do not obey Beer's law, especially at the 0 to 0.9 μg Rh/ml concentrations; but from 0.9 to 2.1 μg Rh/ml MIBK the curves essentially are straight lines (Fig. 3, dotted lines) to 0.02 absorbance at zero Rh concentration, which indicates an interference for solutions containing phosphoric acid. The absorbance, however, of phosphoric acid solutions with 0% rhodium was 0.005 (no MFS) and 0.007 (with MFS).

In calculating the results (Table I), this blank of 0.007 absorbance was subtracted from the samples. Solutions of phosphoric acid (4 and 6% v/v) in MIBK absorb in an AA flame at 343.5 nm. The small blanks observed for these solutions probably result from some unknown nonatomic absorption phenomena (10).

The behavior of solutions containing phosphoric acid is in direct contrast to standard solutions containing ca. 0.9 g HCl/25 ml MIBK which followed Beer's law (Fig. 2, curve C). A slight decrease in absorbance was observed for solutions containing HCl and MFS (curve D). The large enhancement in absorbance observed with phosphoric acid and MFS was not noted with hydrogen chloride. Solutions containing hydrochloric acid with 0% Rh had zero absorbance, but the straight line curve at 0% Rh intersected at 0.003 absorbance. This was considered to be within the experimental error and ignored.

Rhodium analyses for four samples shown in Table I are compared with the colorimetric results. The amount of Rh in MFS was consistently 10 to 20% low when determined by the direct method using MIBK without purified MFS in the standards. Rhodium in MCS was always 10 to 20% high. However, with MFS and hydrogen chloride added to the standards in MIBK, the results for Rh in MFS and MCS generally agreed with the results of rapid acid digestion and colorimetric methods.

Consistently high results were obtained for all samples using MIBK containing H_3PO_4. Possibly some reaction of MFS or MCS and H_3PO_4 forms unknown complexes with Rh and interferes with the aspiration, absorption, and release (10) in the AA flame. At these temperatures, however, the Rh and Rh complexes should be atomic.

Even though the preparation of Rh standards in MIBK containing hydrogen chloride and MFS is time consuming, it does eliminate the 1- to 2-hr digestion, and the method is preferred for determination of Rh in a large number of samples of MFS and MCS. Since the standards with sulfuric acid are readily prepared, the rapid acid digestion procedure is recommended when only a few analyses are required. Also, accuracy is increased when the Rh standards contain an equal amount of the purified fatty product of the sample being analyzed.

ACKNOWLEDGMENT

R.L. Reichert prepared the various samples of methyl formyl and carboxystearate.

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[Received November 18, 1976]