Phosphorus in Oil. Production of Molybdenum Blue Derivative at Ambient Temperature Using Noncarcinogenic Reagents

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ABSTRACT: The determination of phosphorus content in crude and degummed oils, especially soybean oil, is commonly used to monitor the efficiency of the degumming process. Techniques for phosphorus determination are based on calcination of the oil in the presence of zinc or magnesium oxide, followed by phosphomolybdate formation, a subsequent reduction and a spectrophotometric determination of the final product, molybdenum blue. Several reducing agents have been employed, all of which need heating to develop color, and then cooling before the absorbance is measured. The objective of this study was to investigate the use of potassium antimonyl tartrate as a catalyst for the phosphomolybdate reduction with ascorbic acid at room temperature, to evaluate the useful life of reagents, comparative kinetics of molybdenum blue formation (with and without catalyst addition) and the extent of phosphorus recovery, and to compare these results with those from AOCS Official Method Ca 12-55.

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KEY WORDS: Ambient temperature catalysis, noncarcinogenic reagent, phosphorus by spectrophotometry, phosphorus in oil.

Phosphorus determination in oil is based on calcination in the presence of zinc oxide or magnesium oxide, followed by phosphomolybdate formation, a subsequent reduction and spectrophotometric determination of the final product, molybdenum blue.

Color is developed as a result of the phosphomolybdate reduction, a process which, to date, needed heating at boiling for 10 min, followed by cooling, before the absorbance is measured. Stannous chloride (1,2), hydrazine sulfate (3), 1-amino-2-naphthol-4 sulfonic acid (ANSA) (4,5), and ascorbic acid (AA) (4,6,7) have been used as reducing agents.

The Standard Methods for the Examination of Water and Wastewater compared the performance of stannous chloride and AA. The results obtained in collaborative tests with AA showed a reduction of relative standard deviation and relative error (2).

The most important disadvantages of these methods are the limited stability of the reducing agents, heating at boiling point, cooling before absorbance is measured, and the risks of handling hydrazine sulfate, a carcinogenic substance.

The objective of this study is to demonstrate the use of potassium antimonyl tartrate (PAT) (8) as an ambient temperature, noncarcinogenic (9,10) catalyst for the reduction with AA as the reducing agent.

MATERIALS AND METHODS

Materials. AA, anhydrous monobasic potassium phosphate, ammonium molybdate, hydrazine sulfate, and PAT were from Sigma Chemical Company (St. Louis, MO), and the other chemicals used were from Merck (Darmstadt, Germany). All reagents were of ACS reagent grade.

For verification of the proposed method, crude and degummed soybean oils were used, ranging between 324 and 975 ppm and 39 and 190 ppm phosphorus content, respectively. To determine the extent of inorganic phosphorus recovery, refined soybean oil with 2.0 ppm phosphorus was used. The phosphorus content was determined by AOCS method Ca 12-55.

Proposed technique. Reagents. (i) Ammonium molybdate solution (25 g in 175 mL distilled water) was mixed with a cold (4°C) solution of sulfuric acid (280 mL 18 M in 400 mL of distilled water), diluted to 1 L and stored in a plastic bottle. (ii) 5 M sulfuric acid solution. (iii) PAT solution: Dissolve 1.3715 g PAT in distilled water and dilute to 500 mL. (iv) 0.1 M AA solution (3.22 g in 200 mL distilled water) and maintain at 4°C; stable for 1 wk. (v) 50% potassium hydroxide aqueous solution. (vi) Reagent mixture (RM): mix 25 mL ammonium molybdate solution, 5 mL PAT solution, 30 mL ascorbic acid solution, dilute to 100 mL with distilled water, maintain at 4°C, 2 d useful life. (vii) Phosphorus standard solution 50 μg/mL: Dissolve 0.2196 g. KH_2PO_4 with distilled water in a 1000-mL volumetric flask and dilute to volume.

Procedure. Accurately weigh 1 g of oil in a 42-mm diameter, 50-mm high porcelain crucible, add 0.5 g ZnO, and proceed according to AOCS Official Method Ca 12-55 (3) down to item vii inclusive. Take a 3-mL aliquot (for crude oils), or 5 mL (for degummed oils). Transfer to a 25-mL volumetric flask. Add 8 mL RM and dilute with distilled water. Leave at least 10 min and no more than 30 min. Make the spectrophotometric reading at 888 nm with a reagent blank as reference.

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Comparative kinetics of molybdenum blue formation with and without PAT. To determine the rate of the molybdenum blue formation by the proposed technique, a 12.5-μg phosphorus content standard was used. Changes in absorbance at 888 nm were measured against time.

Standardization. A calibration graph was developed by using the proposed method with different standards that contained between 0.5 and 25 μg phosphorus. For each concentration, the determination was carried out in quintuplicate.

Recovery of inorganic phosphorus. Adequate volumes of the K_2HPO_4 standard solution to obtain 0.5, 1.0, 5.0, 10.0, 25.0, 50.0, and 125 μg phosphorus were transferred to porcelain crucibles. Each one was gently evaporated to dryness, and then 1 g refined oil with 2 ppm phosphorus was added. The total phosphorus content was determined by applying both AOCS Official Method Ca 12-55 (3) and the proposed method. Determinations were carried out in quintuplicate.

Verification of proposed technique. Fifteen crude and 15 degummed soybean oil samples were analyzed by both AOCS Official Method Ca 12-55 (3) and the proposed method. Determinations were carried out in quintuplicate.

RESULTS AND DISCUSSION

Selection of optimal wavelength. The absorption spectrum of the molybdenum blue, obtained by applying the proposed method, showed a major peak at 888 nm and a minor peak at 710 nm.

Reagent life. The useful life was evaluated by considering the addition of reagents i, iii and iv, individually or previously mixed. The variation of the absorbance at 888 nm against time is shown in Figure 1. The reagents, individually, had a 1-wk useful life, whereas when pre-mixed, they had only 48 h of useful life.

Comparative kinetics of molybdenum blue formation with and without PAT. Figure 2 shows that, after addition of PAT, the maximum absorbance was achieved at 360 s. On the other hand, without the addition of PAT, even at 1500 s, the absorbance was still increasing. The molar extinction coefficient values obtained with PAT were (Equation 1):

$$E = 2.064 \times 10^4\ M^{-1}\ cm^{-1} \qquad [1]$$

and without PAT,

$$E = 2.7 \times 10^4\ M^{-1}\ cm^{-1} \qquad [2]$$

Standardization. The values obtained by means of the proposed method and their corresponding standard deviation, regression equation, and regression coefficient are shown in Table 1.

Recovery of inorganic phosphorus. The recovery rate ranged between 89 and 103% by the AOCS Official Method (3), and between 94 and 100% by the proposed method (Table 2).

Verification of proposed technique. In crude soybean oils, phosphorus contents ranged between 349 and 975 ppm; while in degummed soybean oils, they ranged between 39 and 190

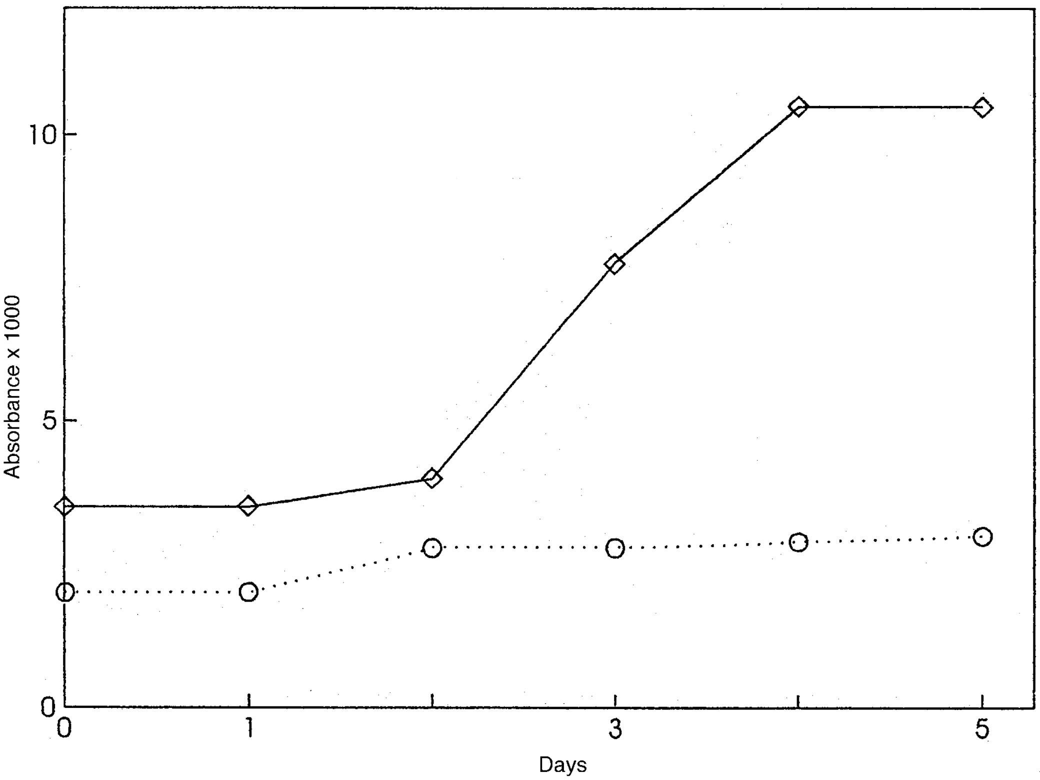

FIG. 1. Variation of reagent absorbance with and without previous mixing of ammonium molybdate, potassium antimonyl tartrate (PAT), and ascorbic acid added previously mixed (◇) and added separately (○).

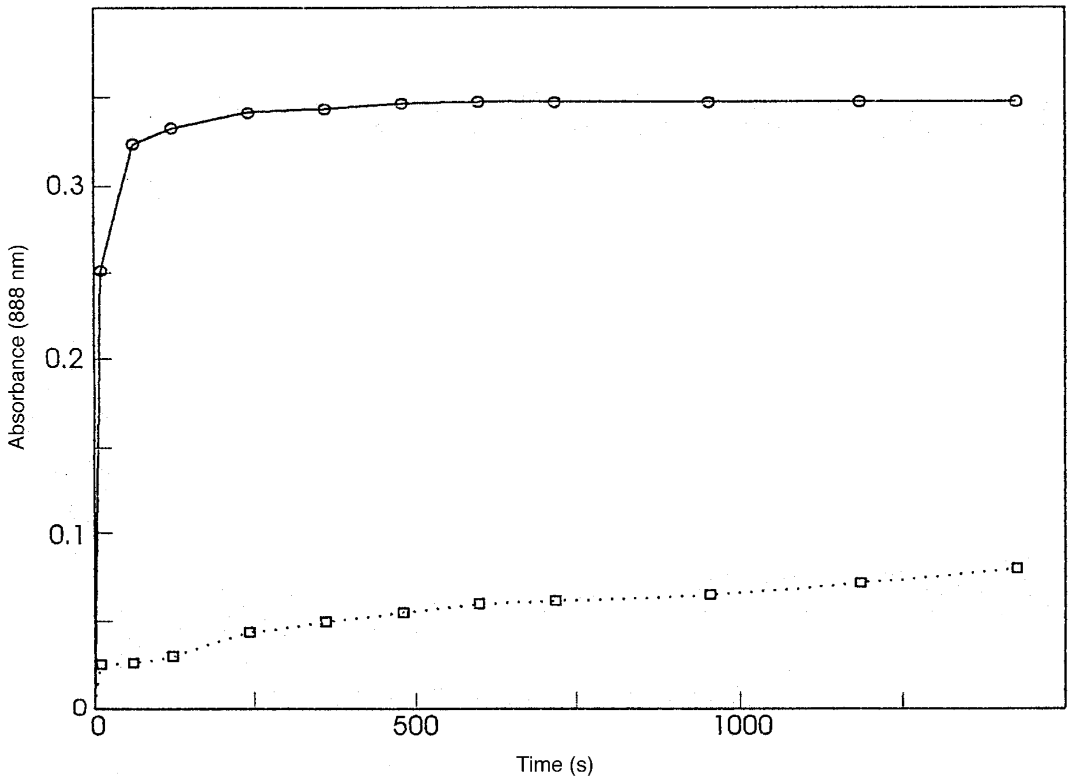

FIG. 2. Comparative kinetics of molybdenum blue with PAT (□) and without PAT (○). See Figure 1 for abbreviation (12.5 μg phosphorus content standard).

ppm. Deviations were calculated from the mean values.The phosphorus content and the relative error between the phosphorus values, determined by the proposed method and by AOCS Official Method Ca 12-55 (3), are shown in Tables 3 and 4, respectively.

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TABLE 1
Mean Values of Absorbance and Standard Deviation by the Proposed Method and the AOCS Official Method

Total phosphorus (μg)	Absorbance at 888 nm	$\delta^a \times 10^3$	Absorbance AOCS Official Method (Ref. 3)	$\delta^a \times 10^3$
0.5	0.0143	0.20	0.0025	0.20
0.2	0.0566	0.60	0.0110	2.20
3.0	0.0846	1.10	0.0180	2.30
5.0	0.1394	2.30	0.0310	2.10
7.5	0.2106	1.10	0.0450	3.00
10.0	0.2738	3.00	0.0500	2.80
12.5	0.3488	1.90	0.0760	2.60
15.0	0.4068	0.80	0.0880	3.20
20.0	0.5438	0.80	0.1170	3.00
25.0	0.6620	1.40	0.1500	4.00

[a] Standard deviation. Regression equation proposed method: absorbance = $6.410 \times 10^{-4} + 0.0266 \times$ μg phosphorus. Regression coefficient: 0.9993. Molar extinction coefficient: 2.064×10^4 M^{-1} cm^{-1}.

TABLE 2
Recovery Rate of Inorganic Phosphorus for Both AOCS Official Method (Ref. 3) and Proposed Method

Phosphorus (μg)	AOCS method recovery (%)	δ^a	Proposed method recovery (%)	δ^a
0.5	97	2.0	100	2.0
5.0	100	2.0	102	2.0
12.5	98	2.0	102	3.0
25.0	92	2.0	98	1.0
50.0	90	2.0	97	1.0
125.0	86	3.0	95	2.0

[a] Standard deviation.

TABLE 3
Phosphorus Content in Crude Soybean Oils Determined by Both the AOCS Official Method and the Proposed Method[a]

	AOCS Official Method		Proposed method		
Sample number	P^b (ppm)	δ^c	P^b (ppm)	δ^c	Relative errror (%)
1	626	4.90	632	5.50	0.96
2	629	4.50	634	4.70	0.79
3	656	4.50	661	5.50	0.61
4	660	4.70	662	5.10	0.30
5	589	5.10	579	6.00	1.70
6	690	3.50	698	5.70	1.16
7	548	4.90	561	4.10	2.37
8	719	2.00	705	5.20	1.95
9	425	4.50	412	4.30	3.05
10	824	6.20	831	5.20	0.85
11	741	4.80	749	3.80	1.08
12	349	4.50	360	5.90	3.15
13	585	6.10	596	3.90	1.88
14	658	3.20	646	3.50	1.22
15	975	3.40	958	5.50	1.54

[a] Standard deviation and relative error of the proposed method compared to the AOCS Official Method.
[b] Five-determination average.
[c] Standard deviation.

TABLE 4
Phosphorus in Degummed Soybean Oils Determined by Both the AOCS Official Method and the Proposed Method[a]

	AOCS Official Method		Proposed method		
Sample number	P^b (ppm)	δ^c	P^b (ppm)	δ^c	Relative errror (%)
16	128	5.00	124	5.20	3.13
17	145	4.90	147	4.30	1.38
18	89	6.30	92	4.80	3.37
19	189	4.30	193	5.40	2.11
20	178	5.30	176	3.90	1.12
21	165	4.80	160	6.50	3.03
22	69	5.90	72	6.00	4.35
23	98	3.60	93	4.50	3.10
24	110	4.40	115	3.90	4.55
25	168	4.50	165	4.80	1.79
26	45	3.90	43	4.40	4.44
27	110	4.80	115	4.30	4.55
28	190	6.50	197	5.50	3.67
29	75	5.70	70	3.80	5.46
30	39	4.80	35	4.20	10.25

[a] Standard deviation and relative error of the proposed method compared to the AOCS Official Method.
[b] Five-determination average.
[c] Standard deviation.

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