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## The Determination of Phosphorus in Different Leathers by Oxygen-flask Combustion

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A HISTORY of the development and uses of the oxygen-flask combustion technique of analysis is presented in the review article by Schöniger.<sup>1</sup> This type of analysis is popular because of its simplicity, ease of operation and the comparatively short time involved in making the determination. It is advisable, however, to observe all safety precautions recommended for combustions of this type. Combustions should be conducted behind a safety glass shield with protective covering for the hands. All combustions in connection with this work were noted to be safe and without incident.

The primary objective of this work was to find a suitable rapid method for determining phosphorus, applicable to the analysis of leather. Initial work showed that when nitric acid was used as the absorbent in the combustion flask, as proposed by Fleischer *et al.*<sup>2</sup> or by Barney, Bergmann and Tuskan,<sup>3</sup> the burning sample produced an objectionable amount of sparking with consequent incomplete combustion and loss of sample. Also, the presence of nitric acid caused erratic colour development with the Association of Official Agricultural Chemists (AOAC) colour reagents.<sup>4</sup> The absorbents suggested by Kirsten and Carlsson<sup>5</sup> were found effectively to suppress spark formation during combustion so that samples were rarely lost by sparking.

The combustion chamber consisted of a regular 500-ml short-necked flat-bottomed flask having a 24/40 ground-glass joint with glass stopper. A hole was drilled in the end of the glass stopper to anchor the wire supporting the sample carrier. Wires extending from the glass stopper and the sample carrier were inter-connected so that they could be disengaged by rotation of the stoppered flask. The sample carrier could thus be completely immersed in the absorbent solution for more efficient dissolution of combustion residues.

Flasks were prepared for the combustion by placing in them 5 ml of 0.8 N sodium hydroxide and flushing with oxygen for about 3 minutes. Seven millilitres of saturated bromine water were then quickly added to the contents of the flask from a pre-calibrated transfer pipette having the tip removed for fast delivery. The fuse of the sample was then ignited and the sample assembly plunged into the flask to ensure a closed seal during and after combustion. After combustion, the sample carrier was demounted into the absorbent and the stoppered flask held for 30 minutes

SHORT PAPERS

with intermittent shaking. The stopper with its wire stem was then washed and removed. Five millilitres of 22 N sulphuric acid were next added, and the contents of the flask with the sample carrier were boiled for 4 minutes over a gas flame. Boiling provided supplementary oxidation conditions, complete bromine removal, and conversion of phosphate complexes to orthophosphates suitable for analysis by the selected colour reagents.

Dependent on the expected phosphorus content in the sample, the entire contents of the combustion flask were transferred quantitatively into a 50-, 100- or 250-ml calibrated flask and made up to the mark. Portions (2, 5 or 10 ml) considered most likely to give full colour development with the colour reagents were placed in separate 25-ml calibrated flasks. Two millilitres of each of the three AOAC colour producing reagents<sup>4</sup> were added to each portion, and the contents of the flasks were then made up to the mark. It was found that 25-ml burettes were satisfactory for adding the reagents, with advantages in speed and convenience over the use of pipettes. However, the AOAC colour reagents are sensitive to high concentrations of acid, and the acidity should be reduced to 21 milli-equivalents or less per 100 ml before the AOAC colour reagents for full colour development are added. Because of the small amounts of phosphorus in the combustion residues of the last three leather samples analysed (see Table I) the acidity was reduced in the combustion flask, the contents were transferred to a 100-ml calibrated flask, 3 ml of each AOAC colour reagent added, and the contents of the flask were made to the mark for colour development. Smaller amounts of colour reagents were found satisfactory for these low phosphorus values and thus a greater volume of water could be used for rinsing and added during transfer of the sample to the calibrated flask.

Readings of the colour intensity developed were made on a Beckman DB spectrophotometer at 650 m $\mu$  against a blank solution treated in the same manner as the sample solution. A standard 1-cm glass cell was used, but the cell was sealed and equipped with conduits to allow it to be operated by a GME Automatic Transferator. Satisfactory conduits were made of intramedic polythene tubing of internal diameter 0.055 inch, external diameter 0.075 inch. About 4.6 ml of sample were found to be a convenient amount for transfer. Flushing between samples was not necessary except when there were wide differences in colour intensities.

It was found convenient and desirable to allow the AOAC reagents to react with the sample for a period of about 2 hours to develop full colour and minimise slight differences in reading times. All readings were compared with a phosphate standard treated under the same conditions as the sample portions, *i.e.*, temperature, size of vessel, milli-equivalents of acid present, reaction time, etc.

Table I lists phosphorus values for three reference standards, *viz.*, Syntropan (amprotropine phosphate; 3-diethylamino-2,2-dimethylpropyl tropate phosphate) triphenylphosphine and triphenyl phosphate, a commercial grade dioctadecyl phosphite and five different sheepskin leathers. These leathers were tanned with a phosphorus-containing compound, tetrakis(hydroxymethyl)-phosphonium chloride, in combination with resorcinol, by Windus, Filachione and Happich's

TABLE I  
PHOSPHORUS DETERMINED IN CHEMICALS AND LEATHERS BY THE CARIUS  
AND PROPOSED METHODS

	Weights of sample used in proposed method, mg	Phosphorus content		
		Theoretical, %	Found by—	
			Carius method, %	proposed method,* %
<i>Chemicals—</i>				
Syntropan .. .. .	4.38 to 7.00	7.64	7.59	7.65
Triphenylphosphine .. .. .	3.96 to 5.49	11.83	11.78	11.85
Triphenyl phosphate .. .. .	6.01 to 6.22	9.51	9.28	9.69
Dioctadecyl phosphite, commercial grade	7.85 to 12.21	5.28	4.63	4.65
<i>Origin of leather—</i>				
United States sheepskin .. .. .	10.40 to 12.00	—	2.68	2.71
Iran sheepskin .. .. .	10.30 to 32.30	—	2.15	2.16
New Zealand sheepskin .. .. .	23.52 to 25.41	—	0.40	0.46
Iran sheepskin .. .. .	27.92 to 29.70	—	0.48	0.48
Iran sheepskin .. .. .	26.46 to 32.73	—	0.42	0.47

\* Standard deviation of the method was 0.025.

#### SHORT PAPERS

method.<sup>6</sup> Phosphorus values obtained by the Standard Carius method<sup>7</sup> correlate with the proposed method. The results obtained on the test substances illustrate the reliability of the proposed method for determining phosphorus content, although the phosphorus is bound in various different molecular combinations.

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