

# SPECTROGRAPHIC DETERMINATION OF PHOSPHORUS IN VEGETABLE OILS USING A PLUNGER-ELECTRODE SPARK EXCITATION TECHNIQUE

By

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Received August 4, 1976

Presented by Prof. Dr. E. Pungor

## Introduction

An important step in vegetable oil refining is to reduce the concentration of compounds liable to segregation. The precipitate upon hydration is the so-called lecithine sludge which contains 10 to 40% of phosphatides (lecithin, kephaline). The hydration process can be followed by the determination of the phosphorus content of oil. Long-life stability of the oil is ensured when its phosphorus content is less than 0.006%. Technological research requires an analytical method for phosphorus determination in the 0.006 to 0.001% concentration range.

Spectrophotometric methods have been suggested as tentative standard procedures for the determination of phosphorus in refined oils [1, 2]. These methods consist in ashing by a laboratory flame in presence of basic magnesium carbonate or magnesium oxide. The product is dissolved in diluted sulphuric acid and the phosphoric acid formed is reacted with a solution containing sodium molybdate and hydrazine sulphate. The colour reaction is completed by heating the sample on a vapour bath during 30 minutes and the absorption of the blue product is measured at 830 nm. Considering 0.001% phosphorus to be the lower limit of measurement, 3.2 g oil should be ashed according to the standard [2]. In order to study the hydration technology, a great number of determinations had to be carried out. The spectrophotometric method described was found to be less convenient for the routine analysis of large series of samples.

In the literature emission spectrographic methods have been suggested for the direct analysis of hydrocarbons. At first we tried to apply a rotating disc, spark excitation technique [3] but its sensitivity was too low to detect phosphorus in vegetable oils. As an alternative a glowing graphite electrode was immersed into mineral oil and the absorbed and decomposed sample was excited by an arc discharge [4]. This method was modified by us as fol-

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lows: 0.4 ml vegetable oil was filled in two parts into the hole of a graphite cup electrode, the oil was burned by flame and excited by a d.c. arc. By this excitation method phosphorus contents above 0.001% could be detected. However, the addition of the internal reference element to the samples could hardly be accomplished with this technique. Further on we studied the direct excitation of the magnesium oxide base concentrates obtained by the standard ashing procedure. For the excitation of the powder samples an injection spark technique was applied using a plunger-electrode device developed in this laboratory [5, 6]. With the use of 1 g oil samples, this excitation procedure satisfied the demands for sensitivity, precision and rapidity. It is noted here that a similar method was previously applied by MATHIS for the excitation of plant solutions dried on graphite powder [7].

### Results and discussion

A developed version of the plunger electrode device is shown in Fig. 1. The rotation speed of the motor shaft can be adjusted between 5 to 15 r.p.m., the optimum depends on the excitation conditions. Water cooling is important only when arc excitation is used. For this injection technique some kind of pulsating discharge, such as interrupted A.C. arc or spark is convenient. The powder sample is injected into the electrode gap by the periodic air turbulence generated by the pulsating discharge. The feed rate of the filling, i. e. the rotation speed of the motor shaft, was selected to cope with the spray rate and to keep a constant sample level in the tube electrode. The rate of spray depends on the grain size and the density of the sample particles but for grains smaller in size than 0.1 mm, the type of the electrical discharge becomes prevalent. The spray rate is much higher with a spark discharge than with an interrupted arc. According to our recent investigations the most suitable spray rate was obtained for a low voltage spark excitation [8] on samples diluted with graphite powder making the tube electrode charge electrically conductive, so that the discharge appears between the charge and the counter electrode. As a result, here the sample particles are vaporized at a higher rate than in the plasma alone.

### Experimental conditions

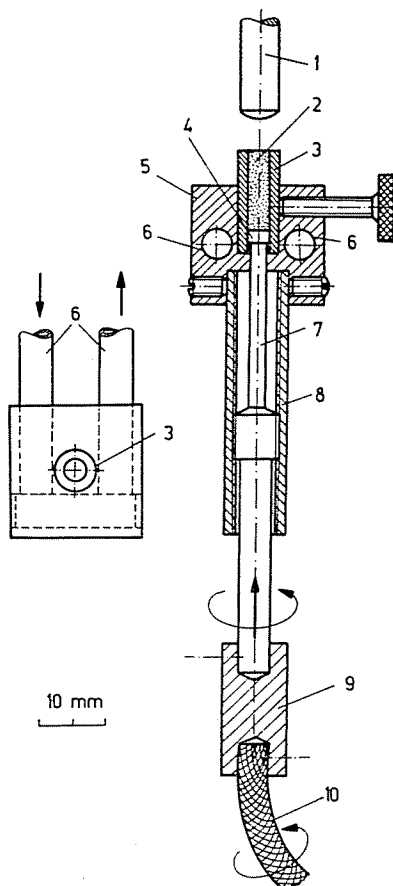
Light source: A.C. arc and low voltage spark generator, FOK-GYEM Model RO-2, 220 V, 30  $\mu$ F, 6 A in short circuit, 100 Hz discharge frequency, 3 mm spark gap. The outer and internal diameters of the graphite tube electrodes were

6 mm and 3 mm, resp., with a length of 25 mm (see Fig. 1). The feed rate of the charge in the tube electrode was 10 mm/min. Both the pre-sparking and the exposure times were 10 s.

**Spectrograph:** ZEISS (Jena) Model Q-24, internal focusing, 0.015 mm slit width. GEVAERT SCIENTIA 34B50 photographic plate and KODAK D 19 developer (4 minutes, 20 °C) were used.

**Microphotometer:** ZEISS (Jena) Model II Schnellphotometer with the use of blackening (S) scale.

**Computer:** RADELKIS, Spectrator (analog computer) converting



*Fig. 1.* Plunger-electrode for the continuous excitation of powdered samples. 1-Graphite counter electrode, 2-powdered sample, 3-graphite tube electrode, 4-stopper made of plastic or cork, 5-copper block, 6-pipe system for water cooling, 7-spindle plunger, 8-brass nut fixed to the electrode holder, 9-isolated contact, 10-flexible shaft connected to the driving motor

the measured blackening values for intensity or concentration. A background correction was applied for the analytical lines of phosphorus.

### Considerations in sample preparation

Magnesium oxide and basic magnesium carbonate have been suggested as additives to oil ashing [1, 2]. Applying basic magnesium carbonate a more effective preconcentration was expected. The thermal processes during the sample preparation were studied by a thermoanalytical method (MOM, Derivatograph). The thermoanalytical curves of basic magnesium carbonate (additive) and magnesium hydrogen phosphate (the supposed product) are shown in Fig. 2. About 100 mg samples were used in the measurements.

The decomposition of the basic magnesium carbonate has four significant temperature characteristics as shown in Fig. 2.

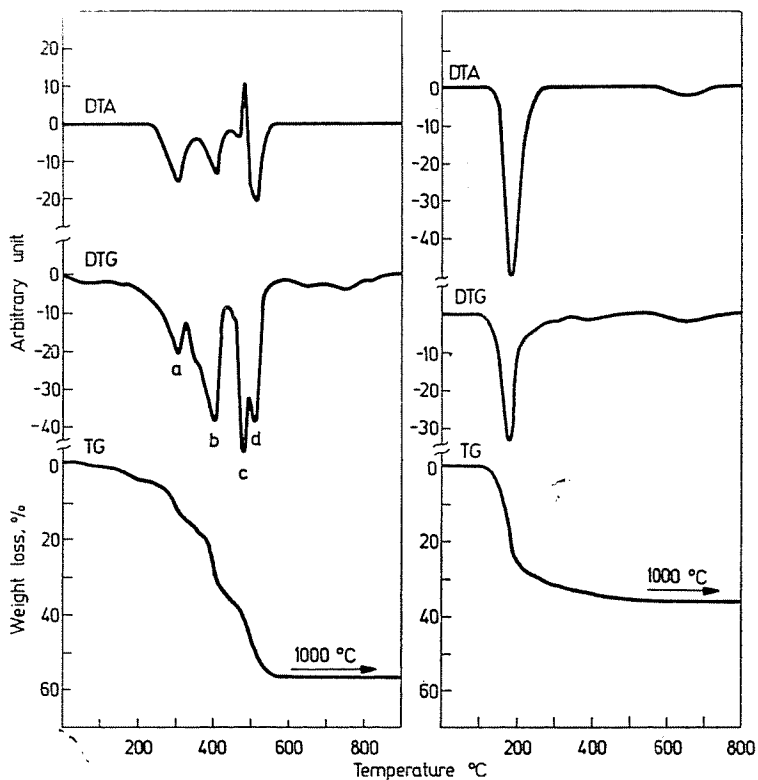


Fig. 2. Thermoanalytical curves. Left — basic magnesium carbonate ( $4 \text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5 \text{H}_2\text{O}$ ), right — magnesium hydrogen phosphate ( $\text{MgHPO}_4 \cdot 3 \text{H}_2\text{O}$ ). TG — thermogravimetric, DTG — derivative thermogravimetric, DTA — differential thermoanalytical curves

*a, b* — evolution of the crystal water (250 to 400 °C)

*c, d* — simultaneous evolution of the chemically bound water and carbon dioxide [9]. The residue above 550 °C is magnesium oxide.

The decomposition rate of magnesium hydrogen phosphate has its maximum at 150 °C but it subsists to 500 °C. According to the stoichiometric calculations, the product is magnesium pyrophosphate ( $Mg_2P_2O_7$ ).

From these curves it can be concluded that the weight of the admixture and the supposed phosphorus compound is constant above 550 °C, and this temperature can be reached using a laboratory flame.

### Preparation of samples

0.2 g of powdered basic magnesium carbonate and 1.0 g oil sample were put into a china crucible of 50 ml, mixed and burned using a Bunsen flame (red colour). The coke produced by the decomposition was combusted in 15 minutes by introducing oxygen gas through a glass capillary into the crucible.

### Preparation of standards

Standards were prepared from lecithin sludge and basic magnesium carbonate. Phosphorus content of 2.48% of the lecithin sludge was found by the standard gravimetric method and a stock solution was prepared with petroleum ether. Variable volumes were added to the portions of an oil sample of low phosphorus content and the solvent was evaporated on a water bath. The heat treatment of the standards was the same as that of the samples (see above).

### Dilution with graphite powder

From preliminary investigations it was concluded that the concentrate obtained by the preparation method described had to be diluted with graphite powder of at least 50% in order to ensure uniform excitation.

The effect to the graphite powder dilution at 50 to 95% was studied using a concentrate with relatively high phosphorus content.

The effect of the graphite powder dilution on the line intensities of phosphorus, magnesium, copper and manganese is shown in Fig. 3. Copper and manganese were present in the oil samples as trace elements. The line intensities are seen not to be proportional to the ash content of the mixture and there

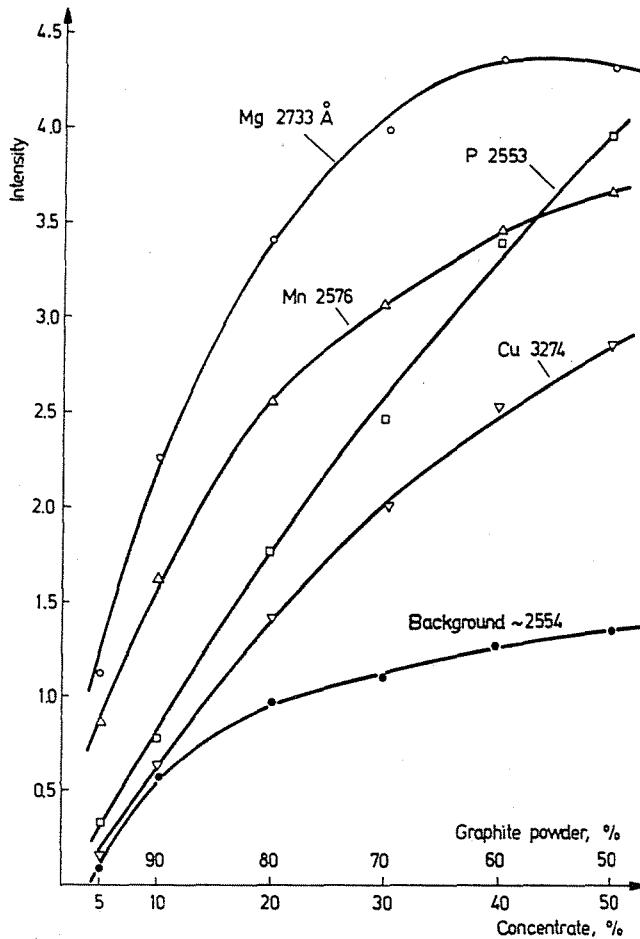


Fig. 3. Intensities of different spectral components vs. admixture composition (concentrate/graphite powder mixture)

is an intensity maximum for magnesium (matrix element). The self-absorption of these lines is negligible so the nonlinearity is interpreted to indicate decrease of the evaporation rate of the sample with decreasing concentration of the graphite powder.

In Fig. 4 the line intensity and intensity ratio characterizing the excitation parameters are plotted as a function of the concentration of the sample-graphite powder mixture. The intensity ratio of the iron ion/atom line pair (excitation index) characterizes the variation of temperature and electron pressure in the spark plasma. This variation is seen to be negligible in the 25 to 50% concentration range of the pre-concentrated sample (i. e. in the range of 50 to 75% graphite powder content).

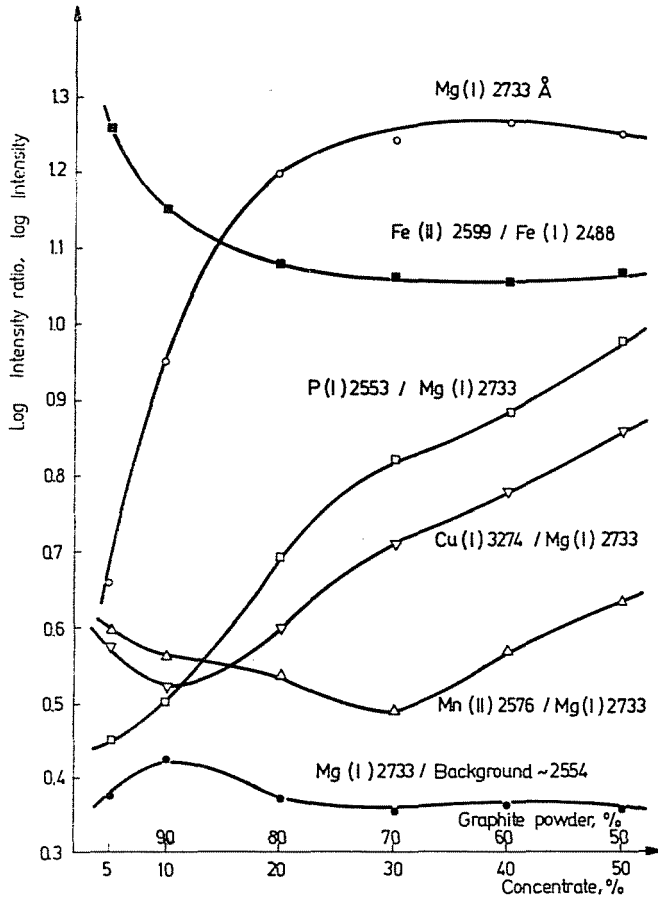


Fig. 4. Intensity parameters characterizing the excitation conditions vs. admixture composition

The line intensity ratios of phosphorus, copper and manganese to magnesium are increasing in this range which means that these trace elements are more volatile than the matrix component. The intensity of the magnesium reference line related to the background intensity measured close to the phosphorus line is constant in the investigated concentration range. This means that the background intensity is determined by the concentration of the magnesium in the plasma, therefore the background could be used as a reference intensity signal. The precision of the phosphorus determination was, however, inferior by a factor of 1.2 when the background was used for this purpose. According to our investigations a graphite powder dilution of about 50% was the optimum for both sensitivity and precision. In the practical work 1 g oil with 0.2 g additive was ashed and the concentrate (96 to 100 mg)

was made up to 200 mg with spectral pure graphite powder and mixed in an agate mortar. About 30 mg sample was filled into the graphite tube electrode and compacted with a steel rod of 3 mm diameter.

### Excitation time studies

The spark excitation with continuous injection has the advantage that the major component can be used as internal reference element even if its volatility differs considerably from that of the elements to be determined. This is shown in Fig. 5 where the log intensity of the magnesium line and the log intensity ratios of the analytical line pairs have been plotted vs. excitation time. The intensity peak of the magnesium line in the initial period corresponds to an irregularly high injection rate into the plasma. After 10 s a constant

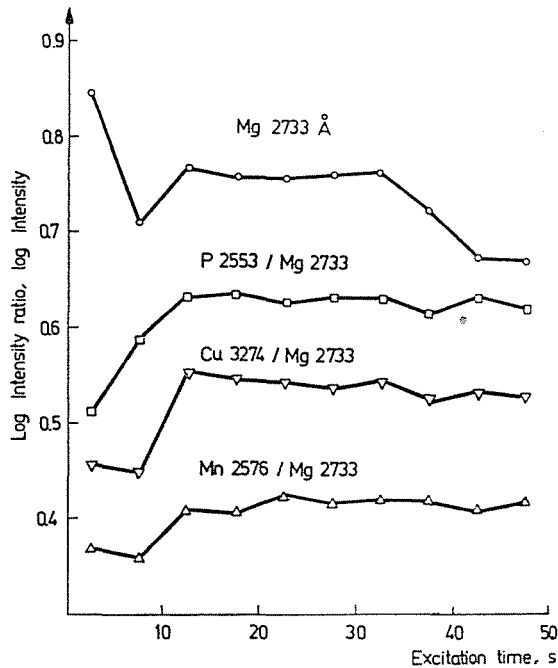


Fig. 5. Sparking-off curves

material level is formed in the tube electrode which results in a uniform injection rate and excitation conditions for about 25 s. With the spectrographic conditions used, 10 s exposure time was, however sufficient from this steady-state period.



### Analytical efficiency

There are two phosphorus lines in the spectrographically well measurable middle UV-range. Under the conditions applied, the P(I) 2535.28 Å line is by 2.7 times higher in intensity than the P(I) 2553.25 Å line. The more intensive phosphorus line might, however, be interfered by an iron line. This interference is negligible on the concentration of iron usually present in vegetable oil samples but it is not when the purity of the additives and the electrodes is not sufficient. The sensitivity requirements were met even by the phosphorus line of lower intensity.

The analytical curve obtained by the standard addition method is shown in Fig. 6. Each point represents an average value of three measurements. No background correction was applied but on the phosphorus line. The curve is linear in a wide concentration range, thus the phosphorus concentration ( $c_x$ ) in the concentrate can be determined with a good accuracy.

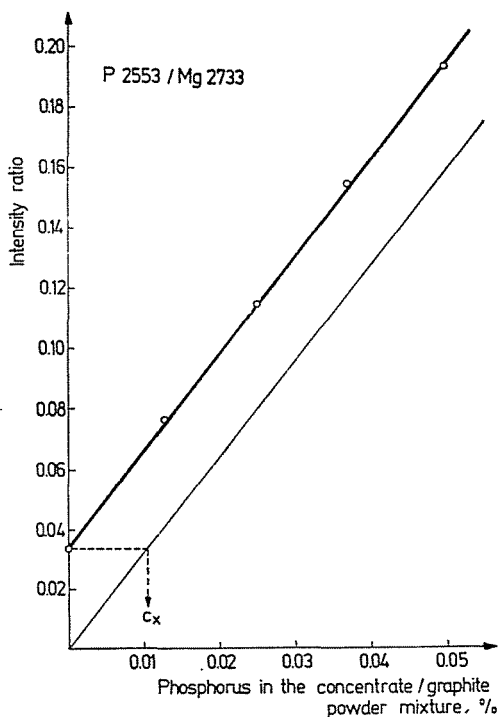


Fig. 6. Analytical curve of phosphorus (standard addition method)

The *detection limit* was calculated from:

$$c_L = \frac{3\sigma(I_B/I_R)}{a}$$

where  $I_B$  is the background intensity close to the analytical phosphorus line,  $I_R$  the intensity of the reference magnesium line,  $\sigma(I_B/I_R)$  the standard deviation of the ratio of these intensities and  $a$  the slope of the analytical curve [8].

Detection limits of 0.0031% and 0.0012% of phosphorus in the concentrate/graphite mixture resulted with the P 2553 and the P 2536 lines, resp. These correspond to 0.00062% and 0.00024% detection limits for the original oil samples.

The *precision* of the determination described was calculated in two different ways. In the first case the relative standard deviation (R.S.D.) was calculated from 38 replicate determinations with the excitation of portions from the same concentrate. The phosphorus content of the oil sample applied was 0.004%, at a R.S.D. of 4.8%. This characterizes the precision of the method, irrespective of the sample preparation error. In the second case seven parts of a given oil sample (0.0032% P) were ashed subsequently, and prepared for excitation. Two determinations were performed from each and the R.S.D. calculated was found to be very close to that in the first method, which means good reproducibility of the sample preparation.

### Summary

An injection spark excitation technique has been developed for the determination of the phosphorus content in vegetable oils by means of emission spectrography. 1 g oil was ashed in the presence of 0.2 g basic magnesium carbonate, the residue was diluted with graphite powder in 1:1 ratio. This admixture was filled into a graphite tube electrode and excited by a low voltage spark using a plunger-electrode device. The calibration was carried out by natural standards, the magnesium matrix element being the internal reference. Detection limit of 0.00062% P and 4.8% R.S.D. in the 0.003 to 0.005% concentration range were found. The technique is also applicable for the determination of some other trace elements (iron, manganese, copper) in vegetable oils.

### Acknowledgements

The authors acknowledge Miss Iona CYRANSKI and Mrs Hedvig PILISI for the precise experimental work.

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