

SHORT COMMUNICATION

Determination of Phosphorous in Rubber by Nitric Acid Digestion

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Currently, a separate digest is required for the analysis of phosphorous (P) in rubber. This involves extra cost and time. Determination of P using the same digest as for all the other elements was tested and compared to the normal procedure. The concentration of P obtained was comparable with coefficient of variation of less than 10%. The regression equation obtained was $Y = 0.996x - 9.28$ with $r^2 = 0.924$, significant at 0.001. The standard error was 0.014.

Based on the results obtained it is thus feasible to analyse P and all the other elements together in a single digestion procedure.

Elemental composition of rubber is routinely analysed at the Rubber Research Institute of Malaysia. Two separate digests are carried out for a complete assay of the inorganic constituents of rubber. One digest, using nitric acid determines the ash, Ca, Mg, Cu, Fe, K, Na and Mn contents while the other which requires pre-ignition and use of sulphuric acid determines the P content. The simultaneous determination of P with all the other inorganic constituents in a single digest reduces labour, cost and time of analysis required for a complete assay of the inorganic constituents of rubber.

Knowledge of the analytical content of P is important since P is an integral component of latex and rubber. Phosphorous has also been indirectly shown to affect latex stability. A higher ratio of Mg to P in latex is one of the contributing factors to latex instability^{1,2}.

Analysis of P in rubber involves the conversion of all forms of P to the orthophosphate form. The orthophosphate is then determined colorimetrically by forming a coloured complex which is

measured at the optimum wavelength of the complex. Several coloured complexes of phosphate can be developed using several chromogens. However, two of the most used and well tested complexes are the phosphorus molybdenum blue complex³ and the yellow complex of ammonium vanadate and ammonium molybdate⁴, they are stable and can be read easily at their optimum wavelengths of 660 nm and 420 nm, respectively.

Since a separate digest is required for P analysis, it was thought prudent to attempt determination of P in solution using the same digest as that for the other elements. This paper reports on the comparative study of the determination of P using a single digest for analysis of all the inorganic constituents in rubber and that by the routine method which involves a separate digest.

EXPERIMENTAL

Materials

Thin films of rubber were made from latices as described in the Manual of

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Laboratory Methods for Chemical Analysis of *Hevea brasiliensis* Rubber⁵.

Methods

Phosphorous in the rubber samples were analysed by two methods viz. the normal procedure (*Method 1*) as described in the Manual of Laboratory Methods for Chemical Analysis of *Hevea brasiliensis* Rubber⁵ and an alternative method (*Method 2*) using the same digest as for the determination of all the other inorganic constituents.

Method 1

Briefly, routine determination of P is carried out by evaporating to dryness 0.1 g of rubber sample with 1 ml of Na_2CO_3 in a porcelain crucible, burning the mixture on a hot plate till smokeless and ashing it at 530°C for 2 h. Re-ashing, if necessary, is carried out by adding another 1 ml of Na_2CO_3 and ashing again at 530°C . To the cooled residue, 1 ml of KNO_3 is then added, evaporated to dryness on a steam bath and the mixture fused by heating on a hot plate. The melt is then dissolved in H_2SO_4 , heated and made up to 50 ml volume.

Phosphate in solution was determined by addition of ammonium molybdate and ascorbic acid to form a blue complex, phosphomolybdenum blue. The phosphomolybdenum blue colorimetric method of determining phosphate in solution is based on the formation of a blue coloured complex obtained by reduction of the phosphomolybdate complex. In acidic condition, ammonium molybdate combines with orthophosphate ions to form phosphomolybdate complex. On addition of a reducing agent, the complex is reduced to form a blue complex, phosphomolybdenum blue which can be measured at a wavelength of 660 nm. In *Method 1*, ascorbic acid was used to reduce the phosphomolybdate complex. The intensity of the blue colour varies with the concentration of phosphate in solution.

Method 2

Ten grams of rubber sample was weighed, wrapped in an ashless filter paper (Whatman No. 542) and ashed in a silica crucible at 530°C . To the cooled ash, 1 ml of concentrated nitric acid was added and evaporated to dryness. If the rubber was not completely ashed, as indicated by its appearance, ashing was repeated for a further 15 min. Another 1 ml of the concentrated nitric acid was added and the mixture evaporated to dryness, 2 ml of dilute nitric acid (20% v/v) was then added and the mixture heated on a steam bath for 30 min. The cooled mixture was then made up to 50 ml volume.

Phosphorous in solution was determined by forming a yellow complex of ammonium vanadate and ammonium molybdate⁶. When an excess of a molybdate solution is added to an acidified solution of a vanadate and an orthophosphate, a yellow complex of $[\text{P}_2(\text{V}_2\text{O}_6)(\text{Mo}_2\text{O}_7)]$ with the ratio of $\text{P}_2\text{O}_5 : \text{V}_2\text{O}_5 : \text{Mo}_2\text{O}_3$ being 1 : 1 : 22 is formed⁶. The complex is stable for a long time and can be measured at a wavelength of 420 nm.

RESULTS AND DISCUSSION

Natural rubber is *cis*-polyisoprene, a hydrocarbon. Phosphorous attached to it can be released by ashing the rubber sample which oxidises the hydrocarbon and converts all the P into meta and pyrophosphoric acids. The rubber can be ashed either directly or by first fusing it with a salt, sodium carbonate. The meta and pyrophosphoric acids formed are converted to orthophosphoric acid by heating with an acid. In *Method 1*, sulphuric acid is used while in *Method 2*, nitric acid is used. Phosphate can then be determined colorimetrically by the development of a stable coloured complex.

The phosphomolybdenum blue method is the more sensitive method of determining P in solution. However, it has been shown that other factors such as acidity, arsenates, silicates and substances that influence the oxidation reduction condition affect the

colour intensity³. In addition, since some of the reagents used for the analysis have limited stability, the blue colour is liable to fade after some time.

Although the yellow phosphovanadomolybdate method is less sensitive, many ions do not interfere even at concentrations up to 1000 p.p.m. The high tolerance to other interfering ions makes the yellow phosphovanadomolybdate a more preferable method of determining P in solution when present in appreciable amounts and in a matrix of several ions.

Result of analyses of 410 rubber samples by the two methods are shown in Figure 1. Values of P obtained by the two procedures are comparable, with coefficient of variation of less than 10%.

The regression equation is $Y = 0.996x - 9.28$ (Figure 1)

where Y = value of P obtained by Method 2
 x = value of P obtained by Method 1

The standard error is 0.014.

The correlation coefficient, $r^2 = 0.924$, significant at 0.001 level.

Statistical *t*-test was carried out on the data with the null hypothesis that the mean P value determined by Method 1 is the same as that determined by Method 2. Based on the analytical data obtained the *t* value computed was 0.78. However, for 408 degrees of freedom at $\alpha = 0.001$, $t = 3.291$. Since the value of *t* obtained, 0.78 is less than $t_{0.001, 408} = 3.291$, the null hypothesis is not rejected. Thus it can be deduced that the mean value of P obtained by Method 1 is not significantly different from that obtained by Method 2. Phosphorous in rubber can thus

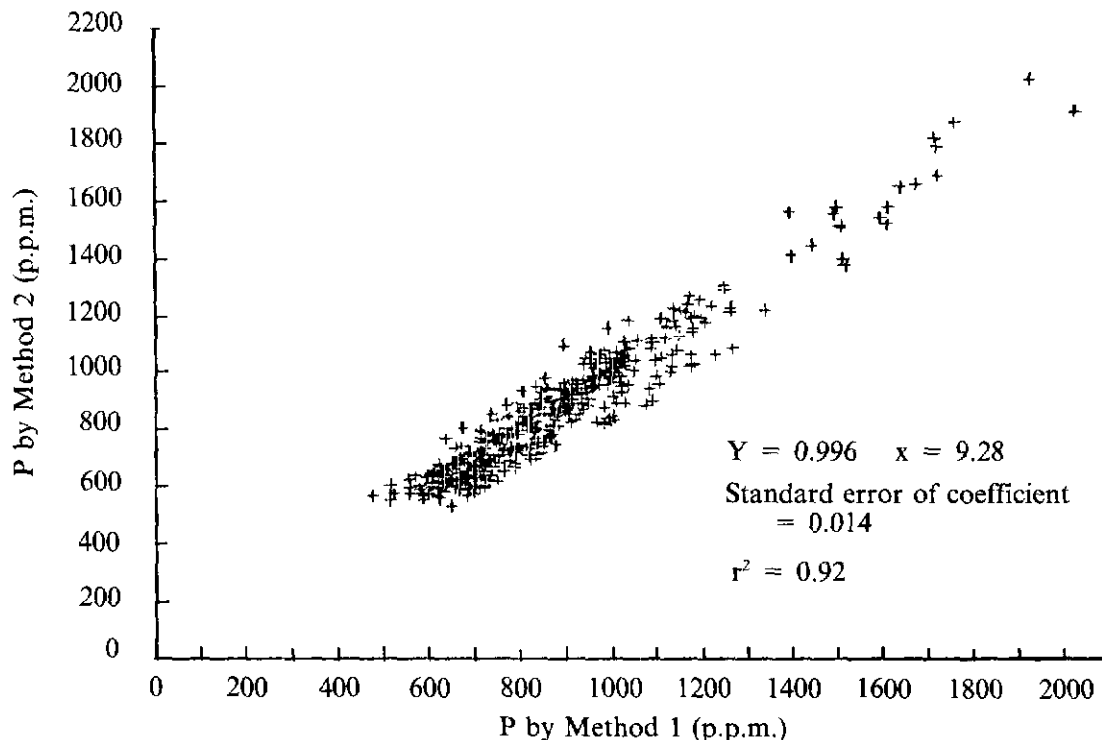


Figure 1. Values of P in rubber samples determined by Methods 1 and 2.

be determined together with all the other inorganic constituents in a single digestion procedure, viz. *Method 2*. This reduces cost, time and manpower required, for a complete assay of the inorganic composition of rubber.

CONCLUSION

Determination of P in rubber by nitric acid digestion is precise and reproducible. The value of P obtained is comparable to P that determined by fusion with sodium carbonate which is the normal procedure. The coefficient of variation is less than 10%. Regression analysis showed that the P values determined by both methods are highly correlated and significant at 0.001 level. In addition, on aliquot of the nitric acid digestion (*Method 2*) can be used for elemental analysis of all the other inorganic constituents of rubber.

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