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QUANTITATIVE DETERMINATION OF FREE ELEMENTAL SULPHUR IN RUBBER VULCANIZATES BY THIN-LAYER CHROMATOGRAPHY

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SUMMARY

A thin-layer chromatographic method is described for the quantitative determination of free elemental sulphur in rubber vulcanizates. The estimation is based on the measurement of the sulphur spot area under specified conditions. Typical results are given for uncured and cured rubbers.

In rubber vulcanizates sulphur exists in several forms, *viz.* (1) combined with the rubber; (2) combined as zinc sulphide; (3) combined in accelerator compounds, their transformation products, and in auxiliary compounding agents; (4) as free elemental sulphur.

Free elemental sulphur (sometimes referred to as 'true free sulphur') arises from incomplete reaction of the elemental sulphur added to the compounded rubber and its quantitative determination is important both in research and process control, as it can be used as a simple chemical test for determining the degree of vulcanization.

Previously used methods are based on the determination of free elemental sulphur in an acetone extract of the rubber vulcanizate by a number of chemical procedures, which form the basis of the British Standard methods.¹ Depending on the method used the result of this determination usually represents an intermediate value between the following extremes: (i) the elemental sulphur extractable by boiling acetone (free elemental sulphur), and (ii) the total sulphur (free elemental and accelerator combined) in the extract. To overcome this difficulty POULTON AND TARRANT² introduced a polarographic method that probably gives the free elemental sulphur in the presence of readily decomposable accelerators, which can be used on a routine testing basis.

In an attempt to reduce the analysis time to a minimum, this problem has now been investigated in a different way by considering the possibility of using a chromatographic technique to separate the acetone extract into its various constituents, in order to isolate the elemental sulphur prior to the quantitative estimation. Previous work^{3,4} carried out in this laboratory showed the usefulness of the technique of thin-layer chromatography (TLC) for the identification of antioxidant and accelerator compounds in vulcanizates, where, by careful choice of the experimental conditions,

free elemental sulphur could be separated and located on silica gel plates using a chromogenic spray reagent consisting of 2,6-dibromo-*p*-benzoquinone-4-chlorimide (1% w/v in ethanol). A more sensitive spray reagent for the detection of sulphur compounds consists of sodium azide in iodine solution as suggested by FINCH⁵. This paper describes the application of TLC and the use of the azide spray reagent to the problem of the quantitative determination of free elemental sulphur in rubber vulcanizates.

EXPERIMENTAL

To establish the optimum conditions for the separation of free elemental sulphur from other components in a vulcanizate extract, preliminary investigations were carried out on silica gel plates using a variety of developing solvents. Good separation was obtained using *n*-heptane as solvent and sodium azide (3% w/v in 0.1 *N* iodine) as spray reagent, a typical chromatogram being shown in Fig. 1.

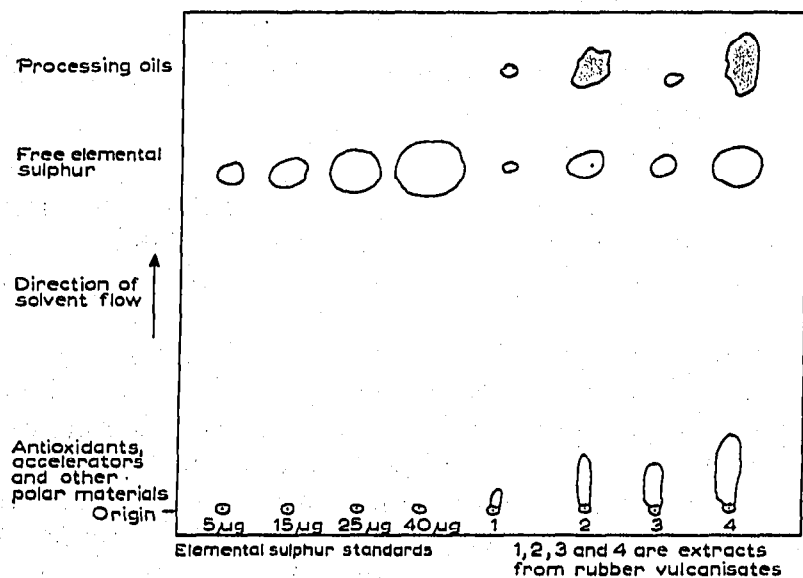
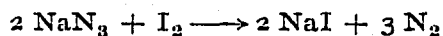


Fig. 1. Typical chromatogram of extracts of natural rubber vulcanisates.

The detection of sulphur compounds by sodium azide in iodine is based on catalysis of the redox reaction⁶



which normally proceeds very slowly. The mechanism of this catalytic effect of certain sulphur compounds has not been completely elucidated and probably involves reactive labile intermediate compounds. The test as described by FEIGL⁷ is normally carried out in solution giving a positive result when bubbles of nitrogen are observed, whereas on TLC plates the detection of sulphur compounds is shown by discharge of the solution colour giving well defined white spots on a yellow-brown background.

METHOD

Summary and explanatory note

The rubber sample is extracted with acetone as in the normal estimation of acetone extract, prior to examination on TLC plates prepared from a slurry of silica gel and water (1:2, w/v) spread onto glass plates using a Shandon applicator.

Reagents

Silica gel, Kieselgel G

Acetone, Analar

Carbon disulphide, re-distilled

Elemental sulphur, recrystallized

Standard solution of elemental sulphur (0.1–0.7 % w/v) in carbon disulphide

n-Heptane, Analar

Sodium azide spray reagent, 3 g sodium azide in 100 ml 0.1 *N* iodine solution

Procedure

The rubber sample is lightly milled to facilitate extraction and 5 ± 0.01 g are acetone-extracted for 16 h under reflux. After removal of the acetone by distillation, the residue is dissolved in carbon disulphide and diluted to 10 ml in a graduated flask. Suitable aliquots (normally 5 μ l) of the extract are pipetted onto a TLC plate using Drummond microcap pipettes, together with the same aliquot of the standard elemental sulphur solutions to cover the concentration range 0–40 μ g sulphur.

The chromatogram is developed in a conventional glass tank lined with filter paper, containing *n*-heptane as developing solvent. When the solvent front has travelled 15 cm, the plate is removed from the tank and dried, prior to spraying evenly with the sodium azide reagent. Free elemental sulphur gives a white spot on an intense yellow background of R_F value 0.7. There is no interference observed from accelerator, antioxidant or processing oil normally used in compounded rubbers. Comparison of spot colour and R_F value for the sample and standards will show whether or not free elemental sulphur is present. The limit of detection is *ca.* 0.2 μ g of sulphur, which corresponds to 0.01 % w/w of free elemental sulphur in rubber, under the experimental conditions previously described.

In order to carry out the quantitative estimation of the free elemental sulphur the spot area is carefully outlined on the TLC plate using a very fine needle, prior to estimating the spot area by tracing onto mm² paper and counting the squares under the spot. A calibration graph is simultaneously prepared from the spot areas of the sulphur standards using the relationship⁸

$$\sqrt{A} = K \log_{10} W$$

where

A = the spot area (mm²),

W = the weight of elemental sulphur applied (μ g),

K = a constant.

A plot of \sqrt{A} against $\log_{10} W$ is shown in Fig. 2, giving a linear relationship over the concentration range 0–40 μg elemental sulphur. The concentration of free elemental sulphur in the rubber extract is calculated by simple arithmetic from the area of the free sulphur spot and the calibration graph for the sulphur standards. The time required for the TLC procedure is 35–40 min.

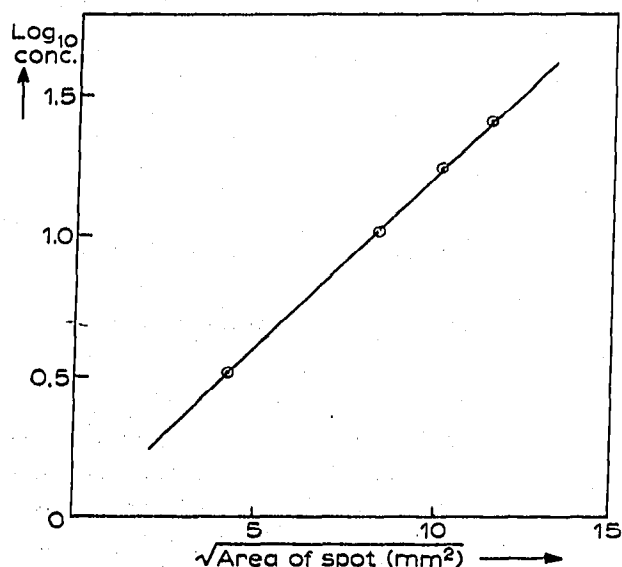


Fig. 2. Calibration graph for elemental sulphur standards.

Possible interference from commonly used rubber compounding ingredients

An exhaustive study of possible interference from the large variety of compounding ingredients used by the rubber industry is obviously impractical and consequently only the more commonly used types have been studied. No interference was observed from antioxidant and accelerator compounds (20 compounds were tested), which all gave R_F values of < 0.1 . Processing oils of the paraffinic, aromatic and naphthenic type gave yellow spots of $R_F > 0.8$ and gave no interference with the sulphur determination at the levels of oil and free elemental sulphur normally found in rubber vulcanizates.

RESULTS

Preliminary results on the precision of the area measurement of the elemental sulphur standards, expressed as twice the standard deviation were better than $\pm 4\%$, provided the experimental conditions were kept constant.

Application to rubber compounds

Uncured rubbers. To obtain samples of known free elemental sulphur concentration, various uncured rubber compounds were prepared and the free sulphur was determined as previously described. The results obtained are shown in Table I, where the precision expressed as twice the standard deviation is better than $\pm 5\%$.

From these results it can be seen that little or no interference is observed from other compounding ingredients.

TABLE I

FREE ELEMENTAL SULPHUR CONCENTRATION IN UNCURED RUBBER COMPOUNDS

| Compound | Free elemental sulphur (% w/w) | |
|--|--------------------------------|-------------|
| | Theoretical | Found |
| Natural rubber/sulphur (milled at 30°) | 2.00 | 2.00 ± 0.05 |
| Styrene butadiene rubber/sulphur (milled at 30°) | 2.00 | 2.02 ± 0.08 |
| Polybutadiene rubber/sulphur (milled at 30°) | 1.68 | 1.57 ± 0.06 |
| Natural rubber latex film | 0.97 | 0.96 ± 0.03 |
| Natural rubber unfilled ^a | 2.26 | 2.23 ± 0.06 |
| Natural rubber black filled ^b | 1.59 | 1.58 ± 0.05 |
| Oil-extended natural rubber ^c | 1.49 | 1.48 ± 0.04 |
| Tyre tread ^d | 1.18 | 1.16 ± 0.05 |

^a Natural rubber 100; ZnO 5; stearic acid 1; sulphur 2.5; accelerator 0.7; antioxidant 1.0.

^b Natural rubber 100; ZnO 5; stearic acid 1; sulphur 2.0; accelerator 0.7; antioxidant 1.0; carbon black 25.

^c Natural rubber 100; ZnO 1.5; stearic acid 0.5; sulphur 2.0; accelerator 0.7; antioxidant 1.0; carbon black 15; processing oil 15.

^d Natural rubber/styrene butadiene 100; ZnO 5; stearic acid 2; sulphur 2.0; accelerator 0.7; antioxidant 2.0; carbon black 55; processing oil 35.

Cured rubbers. To observe whether the technique could be applied to a vulcanized rubber, a typical natural rubber compound was prepared and cured for various times at 140°. Each sample was analysed as previously described, the results obtained being shown in Fig. 3 as a plot of free elemental sulphur against time of cure at 140°.

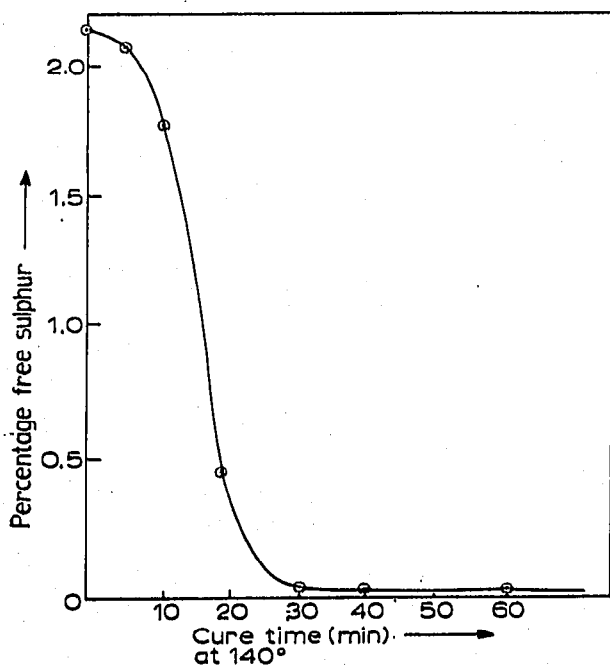


Fig. 3. Graph of free elemental sulphur against time of cure for a natural rubber vulcanisate.

CONCLUSION

The thin-layer chromatographic method offers a rapid and accurate means of determining the free elemental sulphur in vulcanizates. For multiple testing it is much quicker than existing methods since ten extracts can be examined on a single 20 × 20 cm TLC plate in 35-40 min. No interference is observed from the more commonly used accelerators, antioxidants and processing oils.

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