Chromatographic Separation of Accelerator and Sulphur in Elastomer Vulcanisates Using ^{35}S

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The use of tracers *in casu* ^{35}S for determination of concentrations in chromatographic fractions is well established as an expedient means for the location of the peaks in the chromatogram.

It is shown that a simple technique using dry Al_2O_3 as adsorbent allows a quantitative separation of a mixture of free sulphur and accelerators. The sulphur accumulates in the first few ml of eluent and the accelerators follow appreciably later in the chromatogram.

Using labelled accelerators the decomposition of the accelerator during vulcanisation may be followed quantitatively. The activity is determined by scintillation counting in toluene by means of the Packard Tri-Carb Liquid Scintillation Spectrometer. The accuracy of the determination is about 5 %.

In the analysis of elastomer vulcanisates the determination of free sulphur is an important and complicated procedure, especially when a sulphur bearing accelerator is used. Further, in insulating compounds for wires the sulphur is a deleterious element as the sulphur during ageing might react with the copper conductor. Hence amounts of soluble copper compounds can migrate into the elastomer and drastically catalyse the rate of oxidation and consequently the deterioration.

It is therefore attempted to separate sulphur and accelerator by means of a chromatographic technique¹ and the use of ^{35}S as a tracer facilitates the location of the compounds in the eluent.

The recent advent of the liquid scintillation counting technique based upon the fundamental work of G. Reynold, H. Kallmann and F. N. Hayes permits an easy direct determination of the activity in the fractions from the chromatographic column. Here especially the Packard Tri-Carb LS-spectrometer² is very well suited for the purpose.

Fig. 1. Pipetting set up.

Fig. 2. Fractomate and column in a 300 x 20 mm diameter tube.

THE TECHNIQUE APPLIED

^{35}S and labelled accelerator are dissolved in pure toluene. An aliquot part of the solution having, *e.g.*, 10^4 – 10^5 cpm* activity in 2 ml is placed in the chromatographic column by means of the pipetting device shown in Fig. 1. A Carlsberg constriction pipette is operated in conjunction with a hypodermic syringe mounted on a vertical rod by means of an adjustable clamp. A magnifying glass is placed for the inspection of the exact filling of the constriction. All parts of the device are adjustably mounted on the rod.

The column contains a 10 cm filling of dry Al_2O_3 and is placed in the sample collector over the counting vials. In the vials are placed small glass funnels. This ensures that the drops will be safely collected during the shift operation. The active solution is pipetted to the top of the Al_2O_3 and the glass tube washed 3–4 times with small portions of toluene added through a funnel, having a bent tip that touches the glass wall of the column. Finally 30 ml of toluene is added.

First two 1 ml fractions are collected followed by 2 ml fractions until the activity levels off.

* counts per minute.

To the fractions are added 5 ml of toluene containing 5 g 2,5-diphenyloxazole (PPO) and 0.4 g 1,4-bis-2-(5-phenyloxazole)-benzene (POPOP) per liter.

The vials are inserted in the freezer at -3°C and counted after 30 min dark adaption avoiding any exposure to sunlight in the entire procedure.

In the case of elastomer vulcanisates acetone extraction is carried out for 48 h as previously described³. A slight greasing of all ground glass joints in the Soxhlet will reduce losses of acetone to a minimum. The extract is evaporated to dryness and transferred to 25 ml toluene and 2 ml are placed in the column. It is advisable to carry out the extraction and evaporation under N_2 .

For both the basic solution and the fraction internal standard must be prepared either by use of duplicate samples or a repeated counting cycle after addition of activity. This is normally 1 ml of toluene containing 0.2 mg of ^{35}S or a similar amount of the active accelerator. The raw extracts have a yellow colour and show a definite, although not very pronounced quenching.

If the activities of the fractions are added for the peak and this activity divided by the value obtained with the internal standard the amount of sulphur or accelerator is easily computed.

Normally the accuracy will be better than 5 % and fractions of micrograms can be determined within a standard deviation of about 10 %.

Reagents

Toluene, Merck's pure, distilled once in a 300 mm $\times$ 17 mm dia. Klit fractionating column⁴. Stored over CaCl_2 .

Al_2O_3 , Merck's reinst.

S, tetramethylthiuramdisulphide, 4,4'-morpholidedisulphide, Amersham, labelled ^{35}S , initial activity about 500 $\mu\text{Curie/g}$, if not labelled ordinary technical rubber grade chemicals are used.

PPO, *POPOP*, Packard Scientific Instruments Inc.

Fig. 3.

DATA

Ex. 1. Elementary rhombic S-35. As shown in Fig. 3 99.6 % of the activity accumulate in the first 6 ml eluent.

	ml	cpm	%	
Added	2	194 000	100.0	(2.031 mg ^{35}S)
Fractions	0—6	193 308	99.6	
	6—30	679	0.35	

The cut from 6—8 ml is very pronounced.

Ex. 2. Tetramethylthiuramdisulphide (TMT), labelled ^{35}S . Fig. 3 shows 0.02 % activity in the first fraction 0—6 ml, whereas 98.1 % are collected from 19—34 ml.

	ml	cpm	%	
Added	1	309 960	100.00	(0.508 mg TMT- ^{35}S)
Fractions	0—6	60	0.02	
	6—19	785	0.25	
	19—34	304 368	98.2	
	34—67	2 344	0.75	

Thus the separation of the sulphur is quantitative.

Ex. 3. Equal parts of 2-mercaptobenzothiazolyldisulphide and ^{35}S were boiled in toluene 6 hours under reflux. The solution was transferred to 50 ml and 2 ml corresponding to 0.4 mg ^{35}S chromatographed.

	ml	cpm	%
Added	2	87 674	100.0
Fractions	0—6	85 307	97.3
	6—32	574	0.7

It is seen that there is a negligible exchange to MBTS (expected in the fractions 6—32 ml). The ^{35}S is nicely recovered.

Ex. 4. 4,4'-Morpholidedisulphide, labelled S-35. 2 ml corresponding to about 8 mg (63 870 cpm) gave a peak from 20—40 ml containing 66 940 cpm $\approx$ 105 %.

The separation from ^{35}S is safe. The value of 63 870 cpm is low due to the higher amount of quenching in the concentrated basic solution compared to the fractions and the yield can be considered close to unity.

Ex. 5. Thiuram vulcanisates without sulphur. The compound had the following composition:

Hevea Rubber (RSS 1X)	100 parts
ZnO	10
Stearic acid	1
Whiting	54
Clay	52
TMT	2

Vulcanisation was performed at 142°C.

About 1 g vulcanisate was extracted 48 h with acetone, the extract evaporated to dryness and dissolved in pure toluene. From the chromatograms the content of TMT was calculated based upon the activity in the fraction from 6–30 ml, *cf.* Fig. 3.

Vulcanised at 142°C	PHR*TMT	
3'	0.110	added
6'	0.085	2,000 PHR
12'	0.042	
24'	0.033	

It is well known that TMT converts to the zinc salt of dithiocarbamic acid during vulcanisation. The data show that this conversion is fast; *e.g.*, after 3 min vulcanisation only about 6 % TMT remains. The further reaction is approximately a first order decomposition of TMT.

CONCLUSIONS

As the examples illustrate, it is possible to locate the pure compounds in the chromatogram and this knowledge can be used for conventional analysis using non-active compounds. Further, some accelerators and the free sulphur can generally be determined with good accuracy even in extremely small quantities.

An important application of the method is the estimation of exchange reaction between accelerator and sulphur by the introduction of either ³⁵S or labelled accelerators and measurements of the distribution of the activity between initial and later fractions. Some experiments regarding this exchange are described by Blokh ⁵.

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* parts per hundred parts of rubber.