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The gas chromatographic analysis of industrial rubber compositions

A semiquantitative method has been developed for the analysis of industrial rubber compositions using pyrolysis–gas chromatography.

A Perkin Elmer Model 800 chromatograph and the Pyrolysis Accessory of the same firm[1] were used. Twenty-five components were separated by temperature programming and using Apiezon L as stationary phase. Retention data are given in Table I and Fig. 1, where the separation time of isoprene was 2.06 min.

TABLE I

RELATIVE RETENTION DATA WITH RESPECT TO ISOPRENE (2.06 min)

No.	*Compound*	*Relative retention time*
1	Butadiene	0.77
2	Isoprene	1.00
3	a_1	1.61
4	a_2	2.00
5	a_3	2.30
6	a_4	3.31
7	a_5	3.69
8	a_6	4.38
9	a_7	5.00
10	a_8	5.52
11	a_9	5.92
12	a_{10}	6.62
13	a_{11}	7.08
14	Styrene	7.62
15	a_{12}	8.24
16	a_{13}	8.68
17	a_{14}	9.07
18	a_{15}	9.30
19	a_{16}	9.70
20	Methylstyrene	10.1
21	a_{17}	10.6
22	a_{18}	11.1
23	Dipentene	11.4
24	a_{19}	11.8
25	a_{20}	12.5

Experimental

Column packing: Apiezon L, 15 % on Embacel 60–100 mesh
Column length: 183 cm
Column I.D.: 0.32 cm
Temperature programme: 40–120°; 3.3°/min
Injection port temperature: 130°
Pyrolysis temperature: 700°
Carrier gas: argon, with a flow rate of 25 ml/min
Detector: FID.

The method is based on the determination of the relative amounts[2] of five main components: the butene fraction, isoprene, styrene, methylstyrene and dipentene.

For semiquantitative determination peak areas were used; these were calculated from peak height × ½ peak height width. The detector response was taken as unit for all components. The semiquantitative analysis is based on the relative quantity of a single component A_x, which is defined as the ratio of the peak area of one component x to the sum of the peak areas of the five main pyrolytic components. A_B = the butene fraction; A_I = isoprene; A_S = styrene; A_{MS} = methylstyrene and A_D = dipentene. These quantities were calculated from the following equation:

$$A_x = \frac{\text{quantity of component } x}{\text{quantities of butenes + isoprene + styrene + methylstyrene + dipentene}}$$

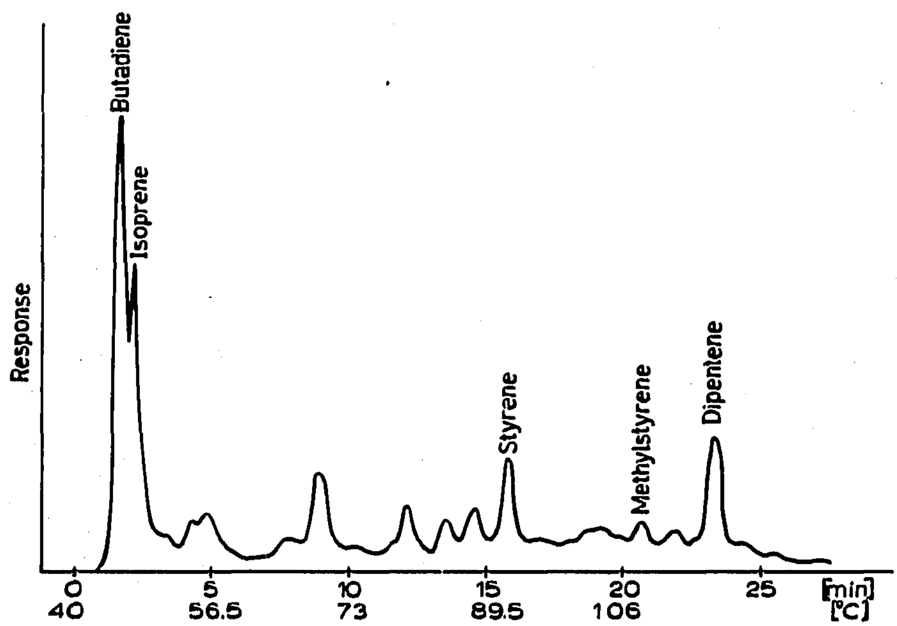

Fig. 1. Pyrogram of the elastomer: RSS-2 25%, SBR-1502 25%, BR-11 50%.

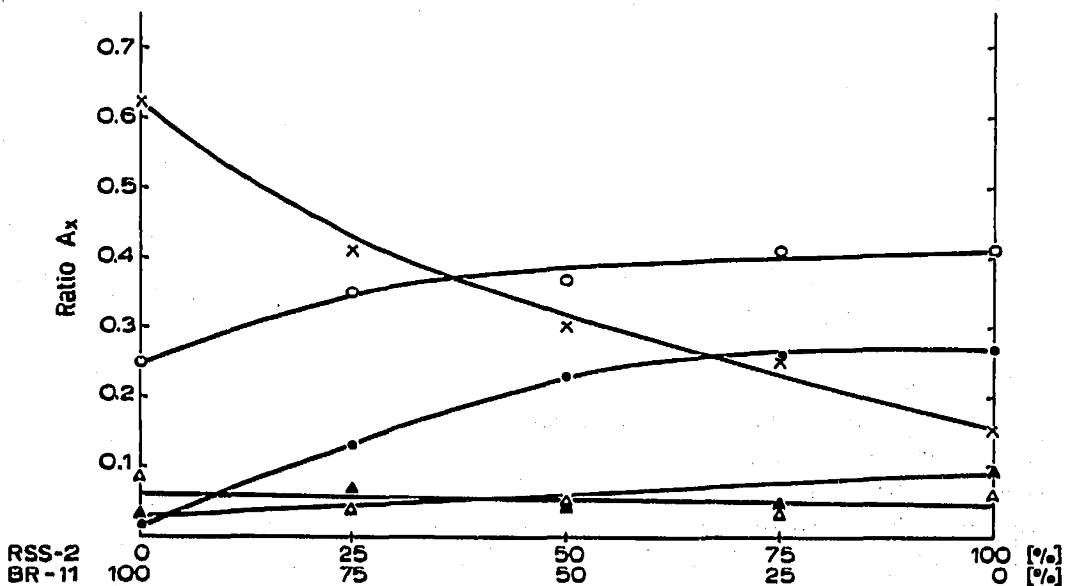

Fig. 2. Standard curves of different compositions of RSS-2 and BR-11. A_B (×); A_I (○); A_S (△); A_{MS} (▲); A_D (●).

Standard curves were plotted from samples of known composition of different stocks of natural rubber RSS-2, 1,4-*cis*-polybutadiene rubber BR-11 (Shell), styrene–butadiene rubber Europrene-1502 (Anic) and high styrene resin KBS-4581 (Chieh, Poland). The standard formulation for these was:

Elastomer	100
ZnO	3
Carbon black: IEP-black (Israel)	48
Antioxidant: ASM-PBN (Bayer)	0.8
Antiozonant: Santoflex IP (Monsanto)	0.7
Accelerator: Vulkacit CZ(Bayer)	1
Stearic acid	3
Paraffin	0.6
Sulphur	2

The samples were extracted with an acetone–chloroform solution 32:68 prior to the pyrolysis. The extraction time was 16 h. The results are collected in Tables II–VI and Figs. 2–6 show the standard curves for different vulcanised rubber stocks.

The method described yielded satisfactory results in the definition of the rubber

TABLE II

COMPONENT RATIOS OF DIFFERENT COMPOSITIONS OF NATURAL AND 1,4-*cis*-POLYBUTADIENE RUBBER

Rubber	*% Composition*				
RSS-2	—	25	50	75	100
BR-11	100	75	50	25	—
Fraction	*Ratios*				
A_B	0.62	0.41	0.30	0.25	0.15
A_I	0.25	0.35	0.37	0.41	0.41
A_S	0.085	0.041	0.049	0.032	0.063
A_{MS}	0.029	0.072	0.047	0.048	0.097
A_D	0.014	0.13	0.23	0.26	0.27

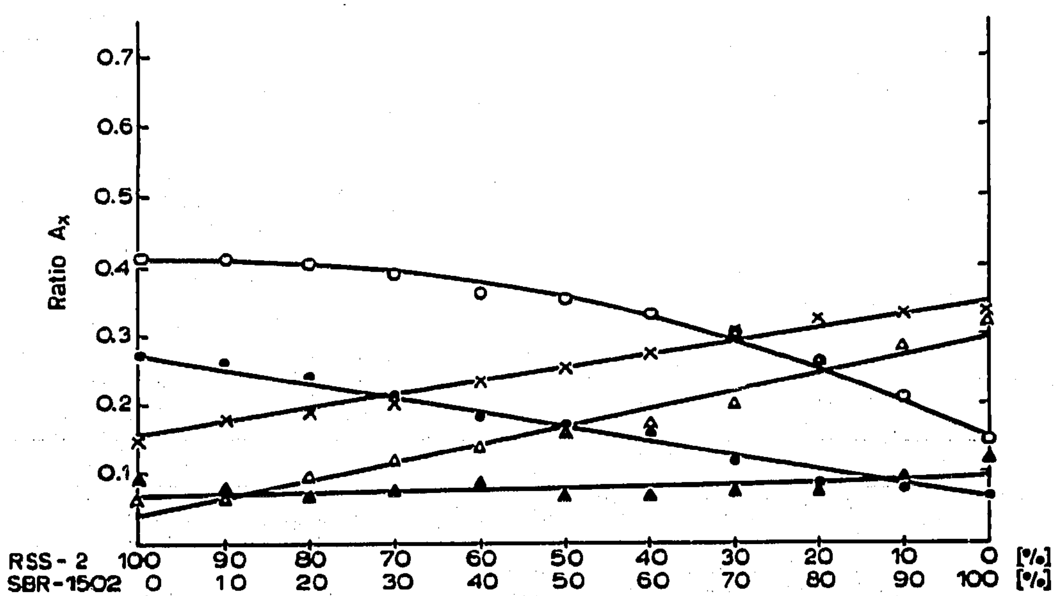

Fig. 3. Standard curves of different compositions of RSS-2 and SBR-1502. A_B (×); A_I (○); A_S (△); A_{MS} (▲); A_D (●).

TABLE III

COMPONENT RATIOS OF DIFFERENT COMPOSITIONS OF NATURAL AND STYRENE–BUTADIENE RUBBER

Rubber	*% Composition*										
RSS-2	100	90	80	70	60	50	40	30	20	10	—
SBR-1502	—	10	20	30	40	50	60	70	80	90	100
Fraction	*Ratio*										
A_B	0.15	0.18	0.19	0.20	0.23	0.25	0.27	0.30	0.32	0.33	0.33
A_I	0.41	0.41	0.40	0.39	0.36	0.35	0.33	0.30	0.26	0.21	0.15
A_S	0.063	0.068	0.096	0.12	0.14	0.16	0.17	0.20	0.26	0.28	0.32
A_{MS}	0.097	0.083	0.073	0.077	0.091	0.070	0.069	0.074	0.078	0.097	0.12
A_D	0.27	0.26	0.24	0.21	0.18	0.17	0.16	0.12	0.083	0.081	0.072

TABLE IV

COMPONENT RATIOS OF DIFFERENT COMPOSITION OF NATURAL, STYRENE–BUTADIENE AND 1,4-*cis*-POLYBUTADIENE RUBBER

(a) *Rubber*	*% Composition*				
RSS-2	—	12.5	25	37.5	50
SBR-1502	—	12.5	25	37.5	50
BR-11	100	75	50	25	—
Fraction	*Ratio*				
A_B	0.62	0.44	0.42	0.32	0.25
A_I	0.25	0.33	0.30	0.32	0.35
A_S	0.085	0.097	0.11	0.12	0.16
A_{MS}	0.029	0.054	0.047	0.052	0.070
A_D	0.014	0.080	0.12	0.17	0.17
(b) *Rubber*	*% Composition*				
RSS-2	—	12.5	25	37.5	50
BR-11	—	12.5	25	37.5	50
SBR-1502	100	75	50	25	—
Fraction	*Ratio*				
A_B	0.33	0.37	0.35	0.35	0.30
A_I	0.15	0.26	0.31	0.28	0.37
A_S	0.32	0.22	0.15	0.11	0.049
A_{MS}	0.12	0.062	0.052	0.056	0.047
A_D	0.072	0.088	0.15	0.21	0.23
(c) *Rubber*	*% Composition*				
BR-11	—	12.5	25	37.5	50
SBR-1502	—	12.5	25	37.5	50
RSS-2	100	75	50	25	—
Fraction	*Ratio*				
A_B	0.15	0.26	0.28	0.40	0.45
A_I	0.41	0.37	0.36	0.26	0.16
A_S	0.063	0.086	0.098	0.16	0.27
A_{MS}	0.097	0.071	0.048	0.079	0.075
A_D	0.27	0.26	0.21	0.10	0.035

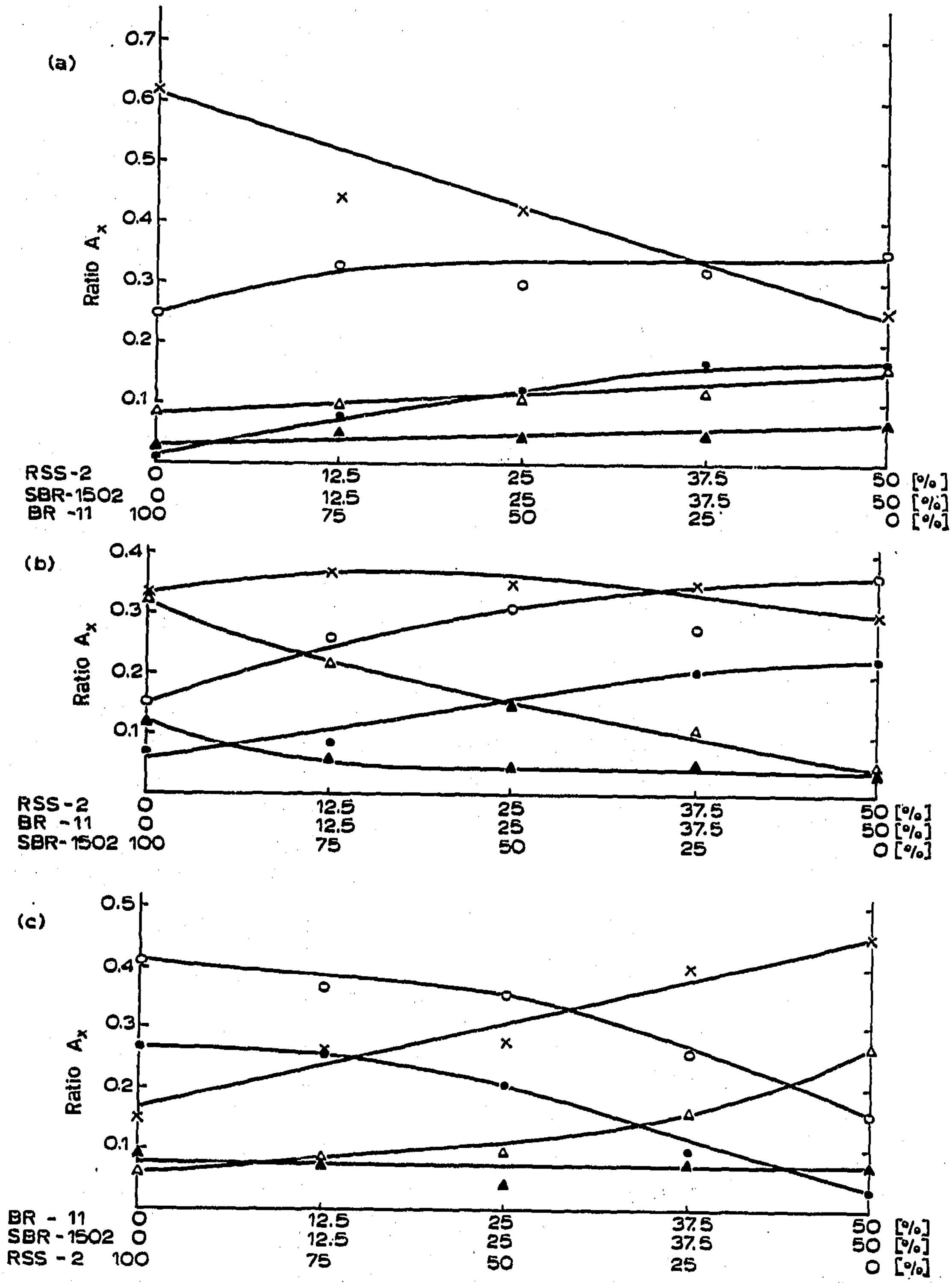

Fig. 4a–c. Standard curves of different compositions of RSS-2, SBR-1502 and BR-11. A_B (×); A_I (○); A_S (△); A_{MS} (▲); A_D (●).

TABLE V

COMPONENT RATIOS OF DIFFERENT COMPOSITIONS OF 1,4-*cis*-POLYBUTADIENE AND STYRENE–BUTADIENE RUBBER

Rubber	*% Composition*				
BR-11	—	25	50	75	100
SBR-1502	100	75	50	25	—
Fraction	*Ratio*				
A_B	0.33	0.41	0.45	0.52	0.62
A_I	0.15	0.13	0.16	0.18	0.25
A_S	0.32	0.33	0.27	0.17	0.085
A_{MS}	0.12	0.086	0.075	0.083	0.029
A_D	0.072	0.047	0.035	0.043	0.014

TABLE VI

COMPONENT RATIOS OF DIFFERENT COMPOSITIONS OF NATURAL, STYRENE–BUTADIENE AND HIGH STYRENE RUBBER

Rubber	*% Composition*				
RSS-2	—	12.5	25	37.5	50
SBR-1502	—	12.5	25	37.5	50
KBS-4581	100	75	50	25	—
Fraction	*Ratio*				
A_B	0.19	0.16	0.21	0.23	0.25
A_I	0.058	0.13	0.19	0.26	0.35
A_S	0.63	0.55	0.41	0.22	0.16
A_{MS}	0.10	0.093	0.082	0.16	0.070
A_D	0.026	0.063	0.11	0.13	0.17

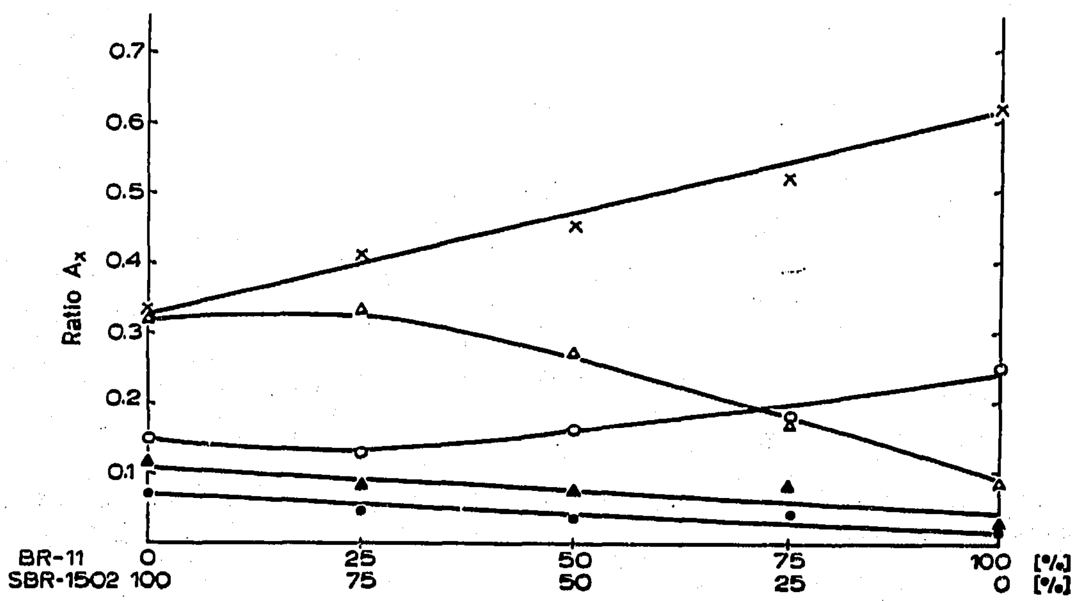

Fig. 5. Standard curves of different compositions of BR-11 and SBR-1502. A_B (×); A_I (○); A_S (△); A_{MS} (▲); A_D (●).

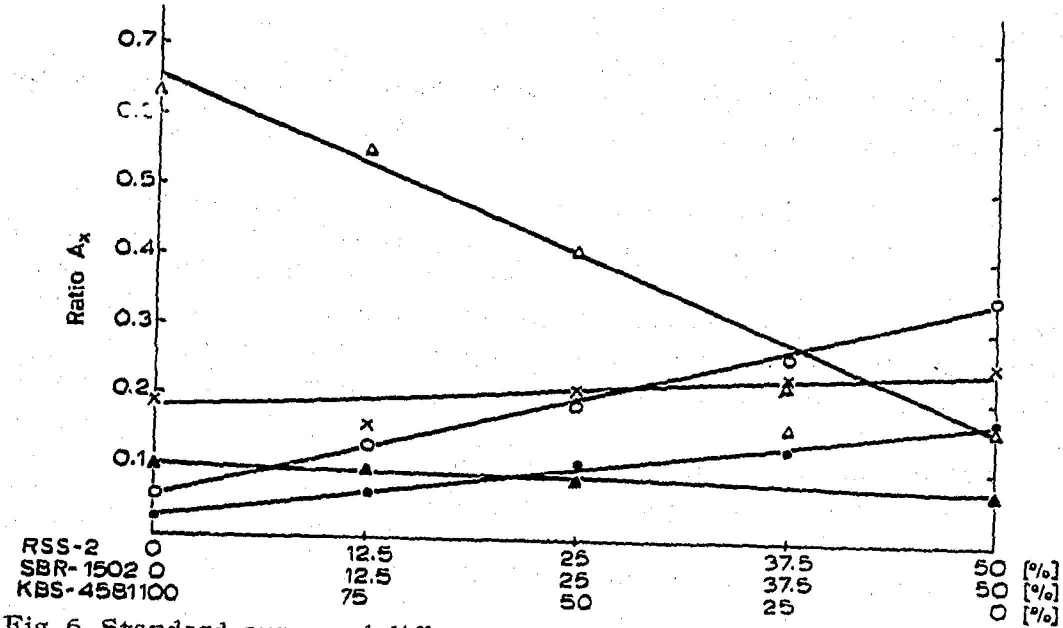

Fig. 6. Standard curves of different compositions of RSS-2, SBR-1502 and KBS-4581. A_B (×); A_I (○); A_S (△); A_{MS} (▲); A_D (●).

composition of the industrial products. The reproducibility was generally good, with σ_{rel} = about 10 %.

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