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DETERMINATION OF WATER AT THE PARTS PER MILLION LEVEL IN BUTA-1,3-DIENE AND ASSOCIATED SOLVENTS BY GAS CHROMATOGRAPHY

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SUMMARY

Water in buta-1,3-diene and associated solvents (such as raffinate oil) can be determined by gas chromatography at levels as low as 1 ppm. The method is mainly based on the excellent selectivity of the porous carbon beads TDX-02, the use of a micro-syringe for liquefied gas, and two criteria for accurate quantitative measurement.

INTRODUCTION

The determination of water, especially at trace levels, is important in many areas, such as in investigations of the activities of catalysts, the separation of gases by deep freezing, the protection of various devices from corrosion and insulating properties in electrical systems.

In the production of *cis*-polybuta-1,3-diene rubber, the presence of moisture in the monomer or solvent (raffinate oil, etc.) will deactivate the expensive catalysts used, and also frequently will cause blockages in the reactor or pipeline. Usually the water content in the monomer and solvents must be maintained below 20 ppm.

The determination of trace amounts of water is difficult, and the methods usually used cannot be used satisfactorily for the determination of trace water in butadiene. In the most commonly used Karl Fischer method[1], water cannot be absorbed completely in the reagents owing to the high volatility of butadiene. Also, the reagents used are toxic. The dew-point method[2] cannot be used because butadiene is liable to condensation. Other techniques, such as use of electrolytic hygrometers[3], methods based on the determination of electric capacity[4] and moisture analysers operated on the principle of the oscillating quartz crystal[5], also fail because butadiene polymerizes readily. The general gas chromatographic (GC) methods cannot be used to detect water at levels as low as 20 ppm in liquid samples[6]. Although techniques for converting water into compounds such as acetylene before GC analysis have been developed in order to increase the sensitivity[7–9], the reproducibility of the rate of conversion is poor.

Recently, porous beads of of styrene–divinylbenzene copolymer[10–13] and CMS activated charcoal[14–17] have been used almost exclusively in the determination of water by GC. However, difficulties have still been encountered when the concen-

tration of water is at the parts per million level, especially when present in lower hydrocarbons. These can be summarized as follows:

(1) lack of an appropriate stationary phase for separating water completely from light hydrocarbons while keeping the water peak sharp and symmetrical;

(2) poor sensitivity and reproducibility of the determination of water when the sample is introduced in the gaseous state with a six-way valve;

(3) serious adsorption of water on the stationary phase and also on the inner surface along the path through which the sample travels; and

(4) contamination of the sample by environmental moisture, which causes errors too large to be neglected in the determination of trace amounts of water.

In this work, by using a new type of porous carbonaceous beads, TDX-02[18], synthesized in our laboratory, excellent separations of water from light hydrocarbons have been obtained. Compared with TDX-01, which is analogous to CMS[16], TDX-02 gives much sharper and more symmetrical water peaks.

A micro-syringe was developed for injecting butadiene in the liquid state. The sample is thus introduced in a much more condensed state and the column efficiency and also the sensitivity of the determination of water are greatly increased.

To overcome the effect of adsorption of water on the stationary phase, two criteria are proposed, based on which suitable operating conditions can be selected to give satisfactory results despite the fact that the adsorption of water on the stationary phase cannot be avoided completely.

EXPERIMENTAL

Apparatus

The experiments were carried out with a Model ST-04 gas chromatograph (manufactured by Beijing Analytical Instrument Factory, Beijing, China), specially designed to meet the requirements of this work. The thermal conductivity detector consists of a four-arm rhenium–tungsten filament, the sensitivity for water determination being $S_{H_2O} = 5 \cdot 10^3$ mV·ml·mg^{-1} (nitrogen as carrier gas). The noise is less than 0.002 mV. In order to shorten the time of analysis and to avoid contamination of the column by high-molecular weight components, the instrument is equipped with a back-flushing device that enables the analysis to be completed within 5 min.

For analysis of water in butadiene, a stainless-steel column of length 1 m and I.D. 3 mm was packed with TDX-02 (60–80 mesh). In the determination of raffinate oil, a 2 m × 3 mm I.D. column of GDX-101 (80–100 mesh) (Second Chemical Reagent Factory, Tianjin, China) was used.

The surface of the inner wall of all columns was thoroughly polished in order to decrease the adsorption of water. As shown in Fig. 1, the effect of a smooth surface of the inner wall on the shape of the water peak is obvious.

Nitrogen dried over silica gel and molecular sieve 5A was used as the carrier gas, with a moisture content of less than 5 ppm (v/v).

The Karl Fischer water analyser was a Model SY-2122-658 (Shanghai Machinery Factory Affiliated to the Ministry of Petroleum and Chemical Engineering, Shanghai, China). The titre of the reagent for water is about 300–500 ppm per milliliter for a sample size of 3 ml.

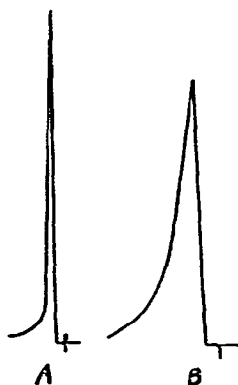The micro-syringe for liquefied gases (Fig. 2) has a zero-dead-volume sliding

Fig. 1. Comparison of water peaks. A, Inner surface of the column well polished; B, inner surface not polished. Sample: $6 \mu l$ of benzene containing $5.45 \cdot 10^{-4}$ mg·ml^{-1} of water. Full scales of the recorder: (A) 8 mV; (B) 1 mV.
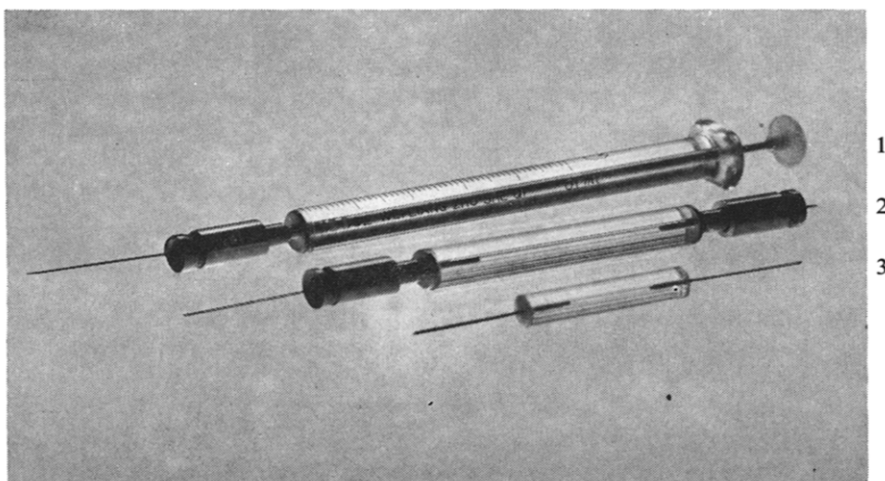

Fig. 2. Micro-syringe for liquefied gases. 1 = Syringe with a sliding valve at the front and a plunger at the back; 2 = syringe with two sliding valves; 3 = needle tube with a glass handle, used for transferring sample from the pipeline to the sample container.

valve at the front, and at the back there is either a similar valve or a plunger with a PTFE washer.

Fig. 3 shows the structure of the sliding valve. A 0.1-mm hole was punched through the wall of the needle tube (I.D. 0.4 mm) of the syringe by means of laser and sealed with a short rubber sleeve. At the moment of taking or injecting the sample, the front sliding valve is pushed so that the rubber sleeve shifts to expose the 0.1-mm hole and the needle tube thus communicates with the capillary tube. As soon as the needle passes through the capillary tube, the liquefied gaseous sample spurts into the sample injection port.

From the equation[19]
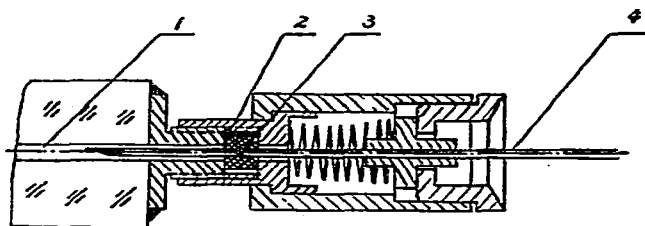
$$\lambda_{eff.} = \frac{T^2 a^2}{12 L k'}$$

Fig. 3. Schematic diagram of sliding valve. 1 = Capillary tube of syringe; 2 = rubber seal; 3 = 0.1-mm hole in the needle tube; 4 = needle tube.

where L is the length of column and k' the capacity factor; the effective plate height of the column, $\lambda_{eff.}$, is proportional to the square of the time for sample introduction, T. By utilizing the micro-syringe for liquefied gases, T is only one-tenth of the time required when using the six-way sampling valve. Thus $\lambda_{eff.}$ is reduced tremendously. This means that the water concentration in the same plate is increased to the same extent and accordingly the sensitivity of the determination is greatly increased. This kind of syringe is able to withstand a pressure of about 6 kg·cm^{-2} with a precision within 5%. Moreover, it is easy to operate and very durable. When it is used in combination with the sample container shown in Fig. 4, a butadiene sample for GC analysis can be obtained in the liquid state without being contaminated by atmospheric moisture.
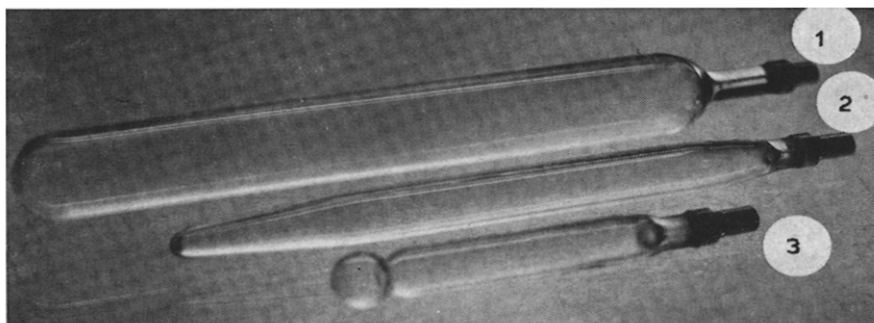

Fig. 4. Sample containers for butadiene. 1 is used in the preparation of standard samples, 2 and 3 are used to take samples in routine analyses.

This syringe can also be used for introducing other gases in the liquid state and some volatile liquid samples, such as isobutane, vinyl chloride, Freons, ethers and even propylene and ammonia.

Chromatographic separation

In raffinate oil, water can be separated well from the solvent for quantitative analysis on GDX-101 styrene–divinylbenzene copolymer beads, but the same packing cannot separate water from light hydrocarbons in butadiene.

The porous carbonaceous beads TDX-01[16] have been used to separate water from light hydrocarbons, but with serious peak tailing, which renders trace

analysis difficult. The new type of porous carbonaceous beads, TDX-02, still retain the good separating characteristics of TDX-01, but are able to elute water before all light hydrocarbons with a symmetrical peak (see Table I). Fig. 5 shows the retention characteristics of water and some other compounds on TDX-02, and Fig. 6 is the chromatogram of water separated from some gases. In Fig. 7, the sensitivity of the determination of water in butadiene is shown to be 3–5 mm (peak height) per ppm of water when 20 μl of liquefied butadiene are introduced, using a 1-mV recorder.

TABLE I

COMPARISON OF WATER PEAKS ON TDX-01 AND TDX-02

Nitrogen gas containing 20 ppm (v/v) of water was used as the sample. The chart speed was 360 mm·min^{-1}. The symmetry of the water peak was measured at one-tenth of the height of the water peak from the bottom; a and b refer to the two parts of peak width separated by the perpendicular drawn from the maximum of the peak to the baseline.

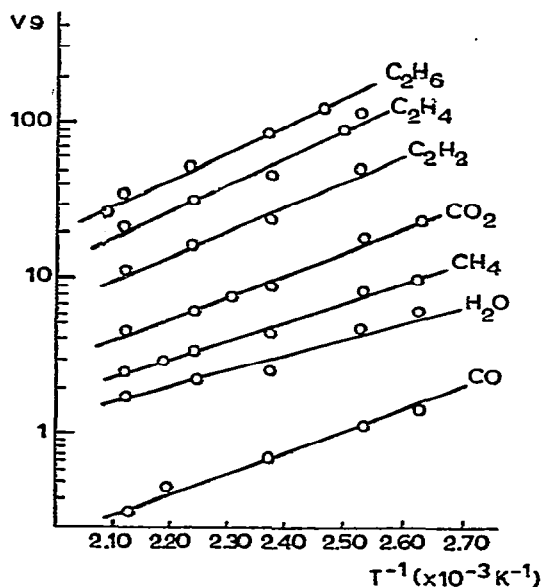| Parameter	Stationary phase	
	TDX-01	TDX-02
Peak width at half-height (mm)	6–8	1.5–2
Symmetry of water peak (a/b)	0.1–0.2	0.3–0.6

Fig. 5. Relationship between logarithms of retention values of compounds in butadiene and reciprocal of column temperature. Column: TDX-02, 1 m × 3 mm I.D. Carrier gas: nitrogen.

Selection of chromatographic operating conditions

Adsorption is one of the main problems in the determination of trace amounts of water. Gough and Simpson[20] found that adsorption of water on the stationary
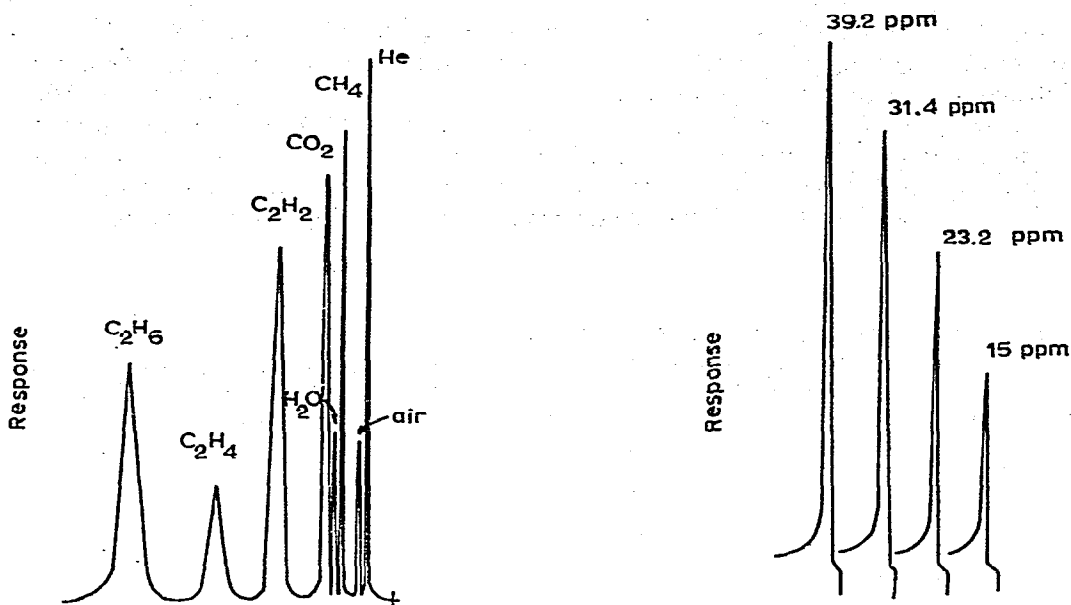
Fig. 6. Chromatogram of some compounds on TDX-02. Column: 1 m × 3 mm I.D. TDX-02 (60–80 mesh). Column temperature: 140°C. Temperature of sample injection port: 273°C. Carrier gas: nitrogen at a flow-rate of 60 ml·min^{-1}. Bridge current: 100 mA. Retention times: helium, 9.7 sec; air, 24 sec; CH$_4$, 54 sec; water, 1 min 18 sec; CO$_2$, 1 min 35 sec; C$_2$H$_2$, 3 min 16 sec; C$_2$H$_4$, 5 min 43 sec; C$_2$H$_6$, 8 min 50 sec.

Fig. 7. Chromatogram of water in butadiene on TDX-02. Conditions as in Fig. 6. Sample size: 21.6 µl. Compounds eluted after water are back-flushed.

phase is the most serious source of error. Moreover, as the absolute water content in the sample increases, the relative loss of water becomes larger.

In this work, it was found that the calibration graph usually does not pass through the origin (A in Fig. 8), but has an intercept on the abscissa or ordinate (B or C, Fig. 8). This phenomenon is caused by adsorption of water on the stationary
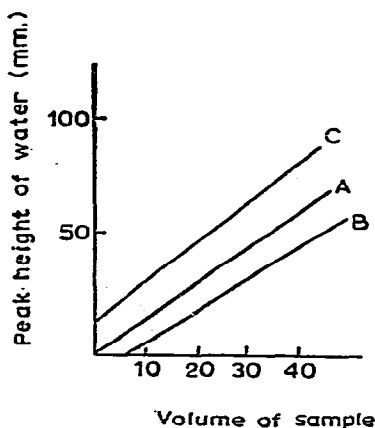

Fig. 8. Intercepts resulting from adsorption of water on stationary phase.

phase, the magnitude of which is usually greater than 10 ppm and is apparently affected by the operating conditions. In order to choose optimal operating conditions, two criteria are proposed, as follows:

(1) The plots of sample volume against peak height of water should pass through the origin, as shown in Fig. 9, where A, B, C and D represent samples with different concentrations of water. In general, this criterion is sufficient for selecting suitable operating conditions. However, sometimes the intercept increases proportionally with increase in sample volume rather than remaining constant. In this instance, although the calibration graphs A, B, C and D appear to pass through the origin, they include a certain amount of adsorbed water represented by curve E, the extent of adsorption increasing with increasing sample size. This happens when an absolutely dry sample is carried over by an excessively pre-heated carrier gas and the adsorbed water is stripped off from the stationary phase. Therefore, the following criterion is also necessary:
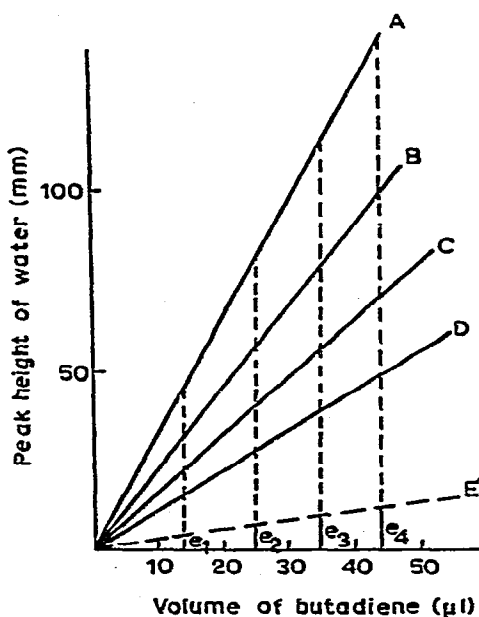

Fig. 9. Illustration of criterion 1. Plots of sample volume against peak height of water. A, B, C and D, samples with different concentrations of water; E, intercept caused by the main component.

(2) The plots of concentration of water against its peak height should also pass through the origin, or should converge at some point along the abscissa, as shown in Fig. 10. Obviously, only when all of the values e_1, e_2, e_3, e_4, ... in Fig. 9 are zero can intercepts of the plots be avoided. At the same time, in Fig. 10 the plots would meet at the origin or at some point along the abscissa.

On the basis of these criteria, we have been able to select optimal experimental conditions (temperature of sample injection port, temperature of column and water content in the carrier gas), as shown in Table II.
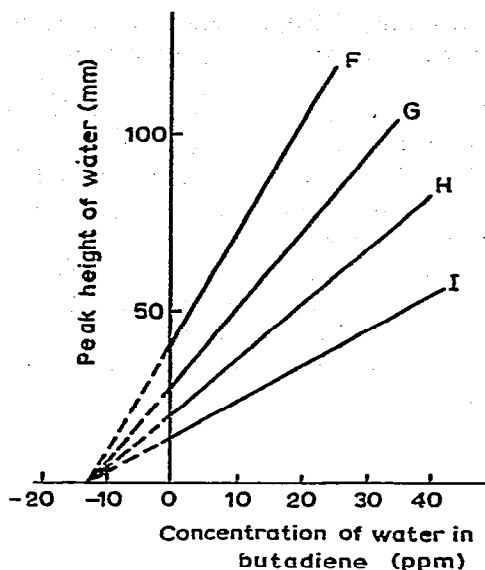
Fig. 10. Illustration of criterion 2. Plots of water concentration against peak height of water. F, G, H, I = Different sample volumes.

TABLE II

CHROMATOGRAPHIC OPERATING CONDITIONS

Sample	Size of column	Stationary phase	Column temperature (°C)	Injection port temperature (°C)	Water content in carrier gas (ppm)
Butadiene	1 m × 3 mm	TDX-02	135–160	250–350	5
Raffinate oil	2 m × 3 mm	GDX-101	120–140	140–250	5

An example can now be given of how the temperature of the sample injection port was selected according to the above criteria. Several temperatures were tested. If the temperature chosen was lower (or higher) than it should be, the plot would neither pass through the origin, as shown in Fig. 11, nor focus at one point, as shown in Fig. 12. Only when the correct temperature was chosen did the plots satisfy the two criteria (Figs. 13 and 14).

RESULTS AND DISCUSSION

On the basis of the above two criteria and by utilizing saturated water in benzene at a definite temperature as the standard[21], a GC method for determinig trace amounts of water in butadiene and raffinate oil was developed. As little as 1 ppm water can be detected within 5 min.

Table III shows the reproducibility of the determination of water in butadiene. In the range of water concentrations tested, the standard deviations were less than 1 ppm.
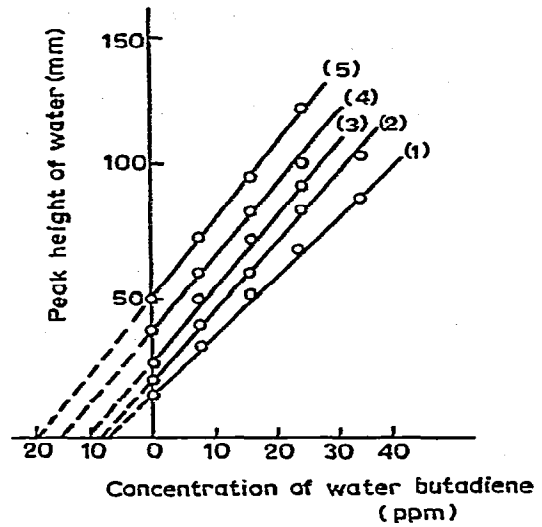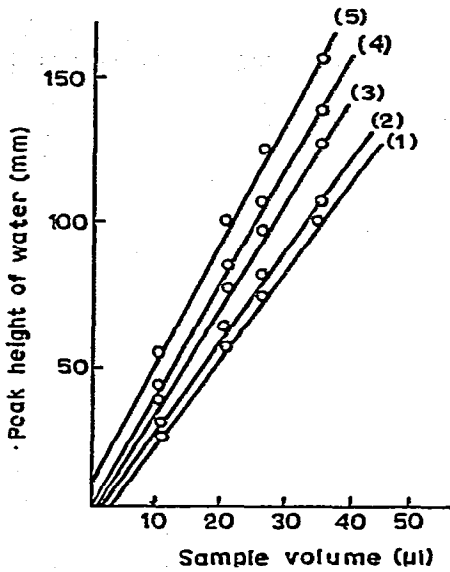
Fig. 11. Selection of temperature of sample injection port according to criterion 1. 1 = 112°C; 2 = 158.5°C; 3 = 199.5°C; 4 = 273°C; 5 = 380°C.

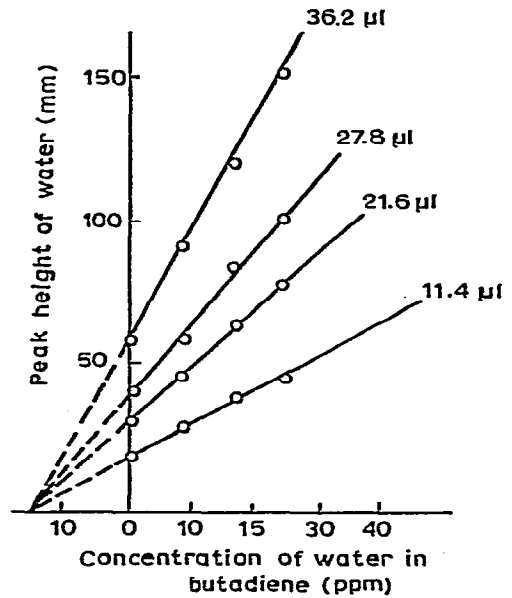Fig. 12. Selection of temperature of sample injection port according to criterion 2. Temperatures as in Fig. 11.
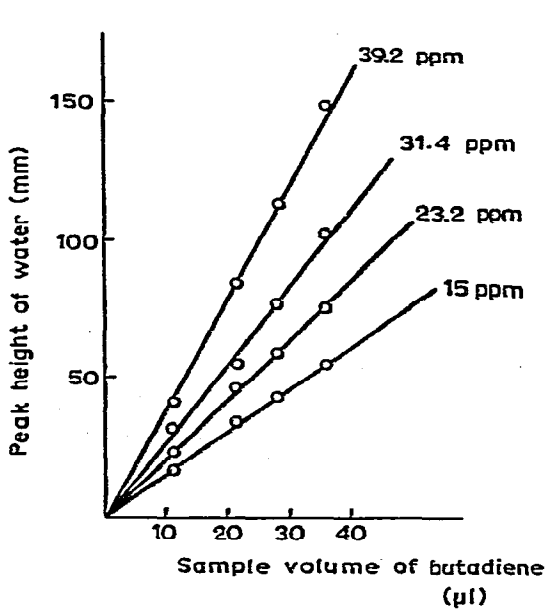

Fig. 13. Relationship between sample volume of butadiene and peak height of water according to criterion 1. Temperature of sample injection port: 273°C.

Fig. 14. Relationship between concentration of water in butadiene and peak height of water according to criterion 2. Temperature of sample injection port: 273°C.

TABLE III

REPRODUCIBILITY OF DETERMINATION OF WATER IN BUTADIENE BY GAS CHRO-
MATOGRAPHY

Four replicate determinations (A–D) were carried out in each experiment.

Experiment No.	Water content (ppm)			
	A	B	C	D
1	14.5	24.1	33.6	41.8
2	13.8	23.4	32.9	41.1
3	15.5	25.1	34.6	42.8
4	15.2	24.8	34.3	42.5
Average	15.2	24.4	33.9	42.1
Standard deviation	0.7	0.7	0.8	0.7

Tables IV and Table V show comparisons between the GC method and Karl
Fischer titration. As can be seen in Table IV, the results obtained by both methods
agree well with the standard. However, with butadiene the results obtained by Karl
Fischer titration are considerably lower than the standard values, whereas those

TABLE IV

COMPARISON BETWEEN GC AND KARL FISCHER TITRATION METHODS FOR
DETERMINATION OF WATER IN RAFFINATE OIL

Standard value (ppm)	Water content by GC method (ppm)	Water content by Karl Fischer titration (ppm)
9.1	9.7	9.6
9.5	8.5	9.6
12.8	13.0	12.0
16.8	16.4	16.0
17.5	16.8	17.4
22.1	23.3	21
44.0	46	45
74.0	76.5	73.5

TABLE V

COMPARISON BETWEEN GC AND KARL FISCHER TITRATION METHODS FOR DE-
TERMINATION OF WATER IN BUTADIENE

Standard value (ppm)	Water content by GC method (ppm)	Water content by Karl Fischer titration (ppm)
9.6	9.2	7.7
12.2	12.4	8.7
13.3	13.5	6.6
19.1	19.5	14.7
23.5	23.6	17.5
25.7	25.6	17.9
28.1	28.0	25.1
35.2	35.6	31.9
37.6	36.4	36.1

obtained by the GC method agree with the standard values (Table V). This may be attributed to the escape of water as butadiene evaporates suddenly during titration.

The method described has been used satisfactorily in synthetic rubber plants for more than 3 years.

ACKNOWLEDGEMENTS

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