Welwyn Garden City Hertfordshire

Telephone Welwyn Garden 23400 (STD Code 07073)
STD Code from London Area 96
Telex 264251 iciplast Welwyn

FEB 18 1974

Chemical Industries Limited

Plastics Division

To: Subcommittee on Analytical Procedures
Technical Task Group on Vinyl Chloride Research
Manufacturing Chemists Association

Your ref	Our ref	Tel ext	Date
			11 Feb 1974

Gentlemen :

Attached are descriptions of various ICI analytical techniques relating to the determination of VCM concentrations in atmosphere, PVC resin, and foodstuffs, for discussion at the Subcommittee meeting in Chicago on the 19th February.

We shall be able to make spare copies of the attached available at the meeting on the 19th but if you feel it appropriate to copy these documents to the other members of the committee in advance, please do so.

A W Barnes

IMPERIAL CHEMICAL INDUSTRIES LIMITED
PLASTICS DIVISION - WELWYN GARDEN CITY

RESEARCH DEPARTMENT
ANALYTICAL DIVISION

The Determination of Vinyl Chloride Monomer in Poly (Vinyl Chloride) Latices, Slurries, Wet Cake and Powders: Solution Injection - Gas Chromatographic Method

Analytical Method P73/8

A R Jeffs
N W Wilson

INTRODUCTION

Two methods are used for the determination of vinyl chloride monomer in poly (vinyl chloride) and in both, analysis is carried out on a solution of the sample in tetrahydrofuran. In the first method, a direct injection procedure is used, whilst in the second, headspace sampling is employed. The former procedure, described here, is a general method applicable to the determination of vinyl chloride in the concentration range 0.01 - 5% in latices and wet cakes as well as powders. It is, however, more suited to the examination of samples having a high monomer content. The sample is dissolved in tetrahydrofuran containing isopropyl chloride as an internal standard. This solution is injected directly into the gas chromatograph for analysis, and the procedure calibrated with known solutions of vinyl chloride monomer prepared in the same internal standard/solvent solution.

APPARATUS

Gas Chromatograph	Fitted with a flame ionisation detector and heated injection port with disposable glass liner. A Perkin Elmer F11 is suitable.
Mechanical shaker	
Volumetric flasks	100 cm^3, 50 cm^3 and 10 cm^3
Conical flasks	50 cm^3, stoppered
Hamilton syringe	10 µl
Micrometer syringe	0.5 cm^3. An Agla syringe is suitable
Pipettes	

REAGENTS AND SOLVENT/INTERNAL STANDARD SOLUTIONS

Tetrahydrofuran	Laboratory reagent grade.
Redistilled Tetrahydrofuran	Reflux the solvent over potassium hydroxide and carefully distil rejecting the distillation foreruns.
Vinyl chloride	Cylinder containing liquid monomer.
Isopropyl Chloride (2-chloropropane)	B.D.H.

Solvent/internal standard Solution A	0.10% v/v solution of isopropyl chloride in tetrahydrofuran.
Solvent/internal standard Solution B	0.01% v/v solution of isopropyl chloride in tetrahydrofuran - prepare by dilution of solution A with redistilled THF.

GAS CHROMATOGRAPHIC CONDITIONS

Set up the gas chromatograph according to the manufacturer's instructions and operate under the conditions detailed below.

Column	4.00 Metres 1/8" OD S/S packed with 20% 'Carbowax', 1540 and 0.5% w/w 'Atpet' 80 on silane (HMDS) treated 'Diatomite C (60-72 mesh).
Column temperature	45°C
Injection port temperature	150°C
Sample size	1 µl
Nitrogen carrier inlet pressure	15 psi
Hydrogen inlet pressure	15 psi
Air inlet pressure	18 psi
Amplifier sensitivity	1 x 20 for low range, 10^2 x 2 for high range.
Recorder	1 mV FSD

CALIBRATION : LOW RANGE : 100 - 2500 µg VC/25 cm^3

Accurately weigh a 50 cm^3 volumetric flask containing approximately 40 cm^3 tetrahydrofuran. Add approximately 1.5 g vinyl chloride liquid and quickly stopper and reweigh the flask. Make the volume up to the mark with tetrahydrofuran, mix, and store in a refrigerator. By means of a pipette transfer 1.0 cm^3 of this solution to a 10 cm^3 volumetric flask containing a little solvent/internal standard solution B. Dilute to the mark with the solution B and mix well. By means of an Agla micrometer syringe transfer 0.10 cm^3 of the second solution to a 10 cm^3 volumetric flask containing a little solvent/internal solution B. Dilute to the mark with the solution B and mix well to give the lower calibration standard, which when prepared from a starting 3% solution contains the equivalent of 750 µg vinyl chloride/25 cm^3 solution.

In a similar manner prepare two other standard solutions containing approximately 1500 µg and 2500 µg vinyl chloride per 25 cm^3 respectively. Calculate the exact strength of each solution.

Set the chromatograph to the appropriate attenuation setting and inject 1 µl of one of the standards. Allow the chromatogram to develop and measure the peak height due to the vinyl chloride and isopropyl chloride. Repeat this procedure for the other standards and in each case calculate the ratio

$$\frac{\text{vinyl chloride peak height}}{\text{isopropyl chloride peak height}}$$

Plot a graph relating these peak height ratios to µg vinyl chloride per 25 cm^3 solution.

CALIBRATION : HIGH RANGE : 2.5 - 25 mg VINYL CHLORIDE/25 cm^3

Accurately weigh a 100 cm^3 volumetric flask containing 80 cm^3 solvent/internal standard solution A. Add approximately 2 g vinyl chloride liquid and quickly stopper and reweigh the flask. Make the volume up to the mark with solvent/internal standard solution A. Mix and store in a refrigerator. By means of a micrometer syringe transfer 0.500 cm^3 of this solution to a 10 cm^3 volumetric flask containing a little solvent/internal standard solution A, and dilute to the mark with solution A to give the highest calibration standard. This, when prepared from a starting 2%.solution contains the equivalent of 25 mg vinyl chloride/25 cm^3 solution. In a similar manner prepare two other standard solutions containing approximately 5 and 10 mg vinyl chloride per 25 cm^3 respectively. Calculate the exact strength of each solution.

Set the chromatograph to the appropriate attenuation setting and carry out the chromatography exactly as described for the low range calibration. Calculate the peak height ratios and plot a graph relating these to mg vinyl chloride per 25 cm^3.

EXAMINATION OF SAMPLES

Dry Powders : Low Range

Accurately weigh an amount of sample not exceeding 1 g and containing less than 2500 µg vinyl chloride monomer into a 50 cm^3 conical flask. Add from a pipette or dispenser 25 cm^3 of solvent/internal standard solution B, immediately stopper the flask and secure the stopper with adhesive tape. Place the flask on a mechanical shaker until the polymer has dissolved, then carry out the chromatography on a 1 µl aliquot of the solution exactly as described for the low-range calibration.

Latices, Slurries and Wet Cake : High Range

Accurately weigh an amount of sample not exceeding 1 g and containing less than 25 mg vinyl chloride monomer into a 50 cm conical flask - Add from a pipette or dispenser 25 cm^3 of solvent/internal standard solution A, immediately stopper the flask and secure the stopper with adhesive tape. Place the flask on a mechanical shaker until the polymer has dissolved, then carry out the chromatography on a 1 µl aliquot of the solution exactly as described for the high-range calibration.

RESULTS

On each sample chromatogram measure the peak height due to vinyl chloride and isopropyl chloride. Calculate the ratio

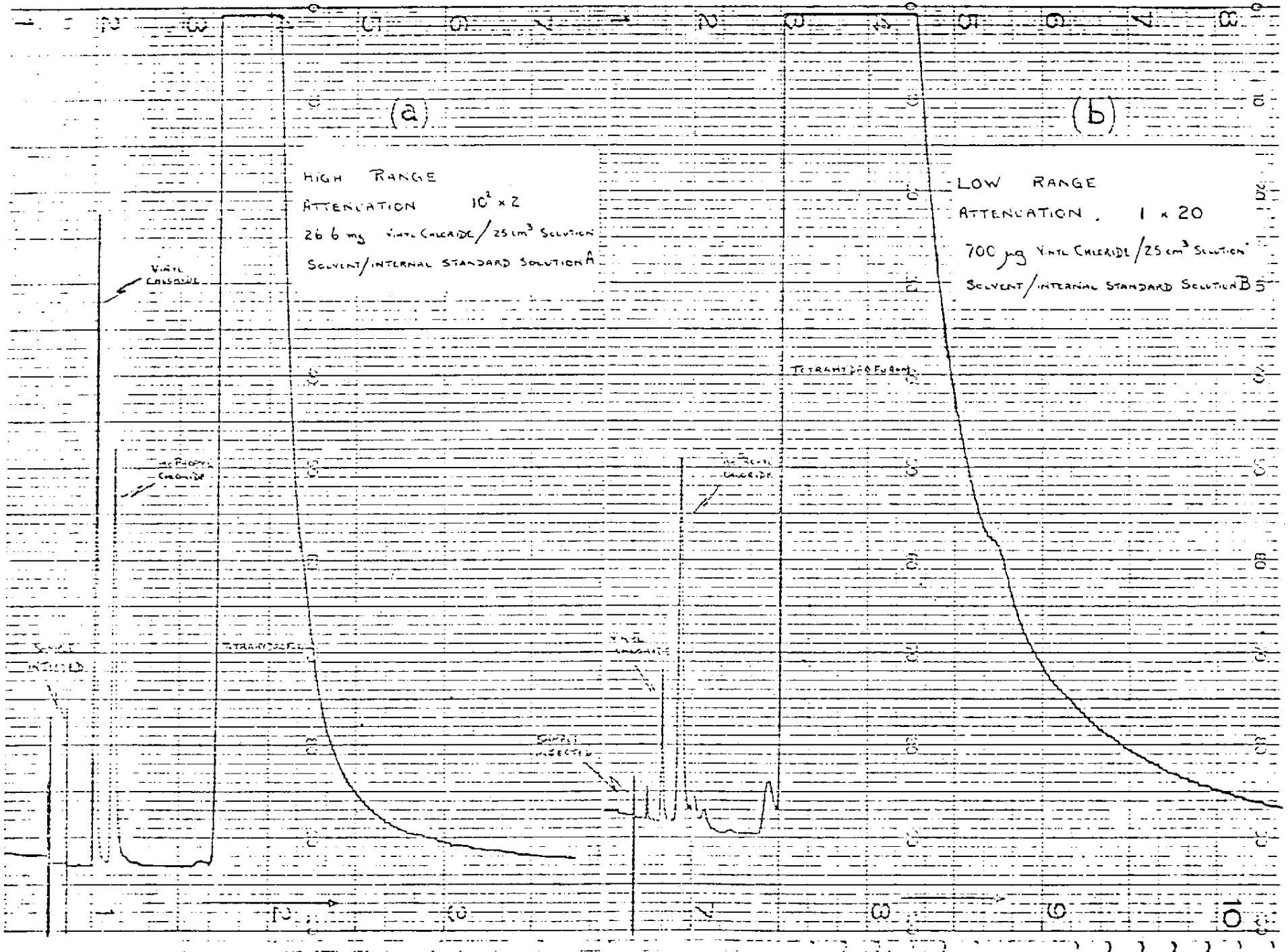
$$\frac{\text{vinyl chloride peak height}}{\text{isopropyl chloride peak height}}$$

and by reference to the appropriate calibration graph read off the equivalent µg or mg vinyl chloride per 25 cm^3 solution. Hence calculate the concentration of vinyl chloride in the original sample and quote the result as parts per million or as a percentage w/w as appropriate.

NOTE

Typical chromatograms are shown in the figure.

5 September 1973
ARJ/DCMS/LEW/R-1/1



IMPERIAL CHEMICAL INDUSTRIES LIMITED
PLASTICS DIVISION - WELWYN GARDEN CITY

RESEARCH DEPARTMENT
ANALYTICAL DIVISION

Analytical Method: P73/9

M R Ringham

The Determination of Vinyl Chloride Monomer in Air

Prototype Analyser using Flame Ionisation Detector

DESCRIPTION OF THE ANALYSER

The analyser has been developed and used for the determination of vinyl chloride monomer concentrations in plant atmospheres. The apparatus consists of a flame ionisation detector, oven temperature controller, amplifier, a gas flow unit and a recorder

Components

The block diagram, Fig. 1, indicates the components referred to below.

A) Heated dual flame ionisation detector head, Pye Series 104, Part No. 791647, modified by removal of one of the flame detectors. (See note 1).

B) Ionisation amplifier Mark II, Pye Series 104, Part No. 791736.

C) Detector oven controller, Pye Series 104, Part No. 791711. Including a silicon rectifier unit incorporated. (See note 2 and Fig. 2)

D) Peristaltic Pump - high flow pump, manufactured by Metering Pumps Limited, Uxbridge Road, Ealing Broadway, London, W.5, using silicon rubber 6 mm bore, 10 mm external diameter.

E) A gas control unit which controls four operations.

1 Fuel gas flowing to the detector.

2 Blank carrier gas flowing through the detector.

3 Introduction of standard gas for calibration.

4 Introduction of the sample gas.

The flow rates in operations 2, 3 and 4 must be the same on entry into the flame ionisation detector. A block diagram of the control unit is shown in Fig. 1..

Operation 1

Hydrogen is piped from a cylinder, using 1/8" copper tubing, to the detector through the gas control unit. The flow rate is regulated by a gauge pressure regulator, R, connected with a Simplex pressure gauge (range 0-5 psi).

Clean air as support gas is piped to the detector through the gas control unit. The flow rate is regulated by regulator, connected with a gauge pressure gauge (0-30 psi). As air is required to flow through the detector

as blank gas when the instrument is in the standby condition the air line is divided: one branch for the fuel gas, the other branch for blank gas.

Operation 2 : Blank Carrier Gas

Air is piped to the '3-way' switch valve X, at position 1. Position 3 at valve X is connected to a '3-way' switch valve Y at position 1. When both valves are in the 'up position' blank air flows through to the detector. The required flow rate of 35 ml/min is obtained by placing a standard restriction between the detector and the Watts regulator T of glass capillary, 0.2 mm bore and 23 cm long. The flow rate is indicated by a Simplex pressure gauge (0-30 psi) connected to regulator T.

Operation 3 : Standard Vinyl Chloride Gas Mixture

The standard gas mixture is piped from a cylinder to valve X at position 2, and then by the same valves and restriction to the detector as in Operation 1. When valve X is placed in the 'down' position the standard gas mixture flows to valve Y which is left in the 'up' position and passes to the detector. (Introduction of blank air and standard gas is from cylinders and therefore on a pressure basis).

Operation 4 : Introduction of Sample

The bellows containing the sample gas is connected at inlet M which is connected through a filter, consisting of a 2" x 1/4" OD glass tube filled with cotton wool, to the peristaltic pump N. The pump is connected to valve Y at position 2 using stainless steel capillary tubing. With valve Y in the 'down' position the sample gas passes to the detector. The pump and connecting lines can be purged with air by switching valve Y to the 'up' position and leaving the pump running.

3) Recorder, Smiths Servoscribe, Type RE 520.20 with a modified scale 0-700.

Note 1

A heated head is essential to prevent the water formed by combustion at the flame tip condensing within the detector and giving rise to considerable electrical noise. Also any hydrogen chloride formed due to the combustion of vinyl chloride would form hydrochloric acid in the presence of moisture and cause serious corrosion within the detector.

Note 2

The electrical control unit is normally mounted at the rear of the analyser oven. An analyser oven is not required for the vinyl chloride detection therefore the silicon control rectifier unit for the detector oven has been incorporated in detector oven controller unit. This circuit diagram should be used in conjunction with Fig. 312.8 detector oven controller Cat. No. 122 04/2 of the Pye 104 chromatograph technical manual.

OPERATING INSTRUCTION

1 Calibration of Flow Rates through the Detector

Flow rates for each gas through the detector are calibrated against the pressures indicated on the gauge by setting these to the required rate using the soap bubble technique and noting the pressure. The optimum rates are:

Hydrogen	30 ml/min
Air	400 ml/min
Sample) Vinyl chloride standard) Blank air)	35 ml/min

2 Settings on Analyser

Detector oven controller setting	Temp. 100-120°C.
Amplifier setting	Attenuator 1? x 10^2. Backing off range x 1. Polarity A Backing off X
Gas flow unit setting	Switch valves X and Y in the 'up' positions.

3 Lighting Flame Ionisation Detector

Switch on recorder.

Turn on hydrogen and air supplies.

Pressure at hydrogen cylinder regulator - 3 kg per sq cm.

Pressure at air cylinder regulator - 2 kg per sq cm.

Turn sample regulator T - off.

Reduce air pressure to 10 lbs per sq in.

Adjust hydrogen pressure reading to 9 lbs per sq in.

Remove cover from flame ionisation detector unit.

Press ignite switch, check flame is alight by placing a polished surface to the chimney of the detector to show condensation. When lit increase air pressure to 15 lbs per sq. in. Adjust regulator T to approximately 4 lbs per sq in.

Replace cover on flame ionisation detector unit.

VVC 000000944

4 Calibrating Analyser

Set recorder speed at 120 mm/hour and millivolt setting at 2 mv.

Open standard vinyl chloride/air cylinder.

Switch from blank gas to standard gas at switch valve Y.

Adjust sample pressure at regulator T to give a recorder read-out for the concentration in ppm v/v of the standard gas mixture being used. . . . Ok ppm v/v. Allow instrument to stabilise over a period of 5 minutes.

When reading is stable turn gas stream from standard gas to blank gas at switch valve X.

The instrument is now calibrated and ready for sample runs. Turn off standard gas mixture at cylinder.

Lock gas control regulators R, S and T.

5 Sampling

The air sample is taken using Fletcher bellows (air sampling aspirator - Gallenkamp Cat. No. GF 430). If an extension lead is required for sampling polyvinyl chloride tubing is used since this does not absorb vinyl chloride monomer. The bellows are filled and emptied three times before taking the sample.

Connect the bellows at M. Switch on and run the pump for one minute. Switch valve Y to down position and run instrument for three minutes or until a stable reading is recorded. Read off in ppm v/v vinyl chloride present from the recorder scale. After the reading has been taken switch valve Y to 'up' position. When the recorder pen has returned to zero the apparatus is ready for the next sample.

Sensitivity

The analyser is capable of measuring vinyl chloride concentrations down to 10 ppm v/v at the standard attenuation setting of 10×10^2 and a pressure setting of 4 psi. The limits of detection on the 10^2 attenuation range are from 1 ppm v/v to 1000 ppm v/v of vinyl chloride in air at the same pressure setting.

PREPARATION AND STANDARDISATION OF VINYL CHLORIDE/AIR MIXTURE

The recommended mixture for calibration is 150-200 ppm v/v in air.

Preparation

A cylinder is evacuated and a calculated volume of vinyl chloride gas is drawn into the cylinder using a gas burette. The cylinder is then brought to atmospheric pressure by allowing air to be drawn at a flow rate of 900 ml a minute. The cylinder is then pressurised to 1400 psi using a compressed air cylinder at 2000 psi. The cylinder is then allowed to stand for at least 24 hours to equilibriate. The vinyl chloride is then determined against a known standard mixture of vinyl chloride in air by gas chromatography.

Standardisation

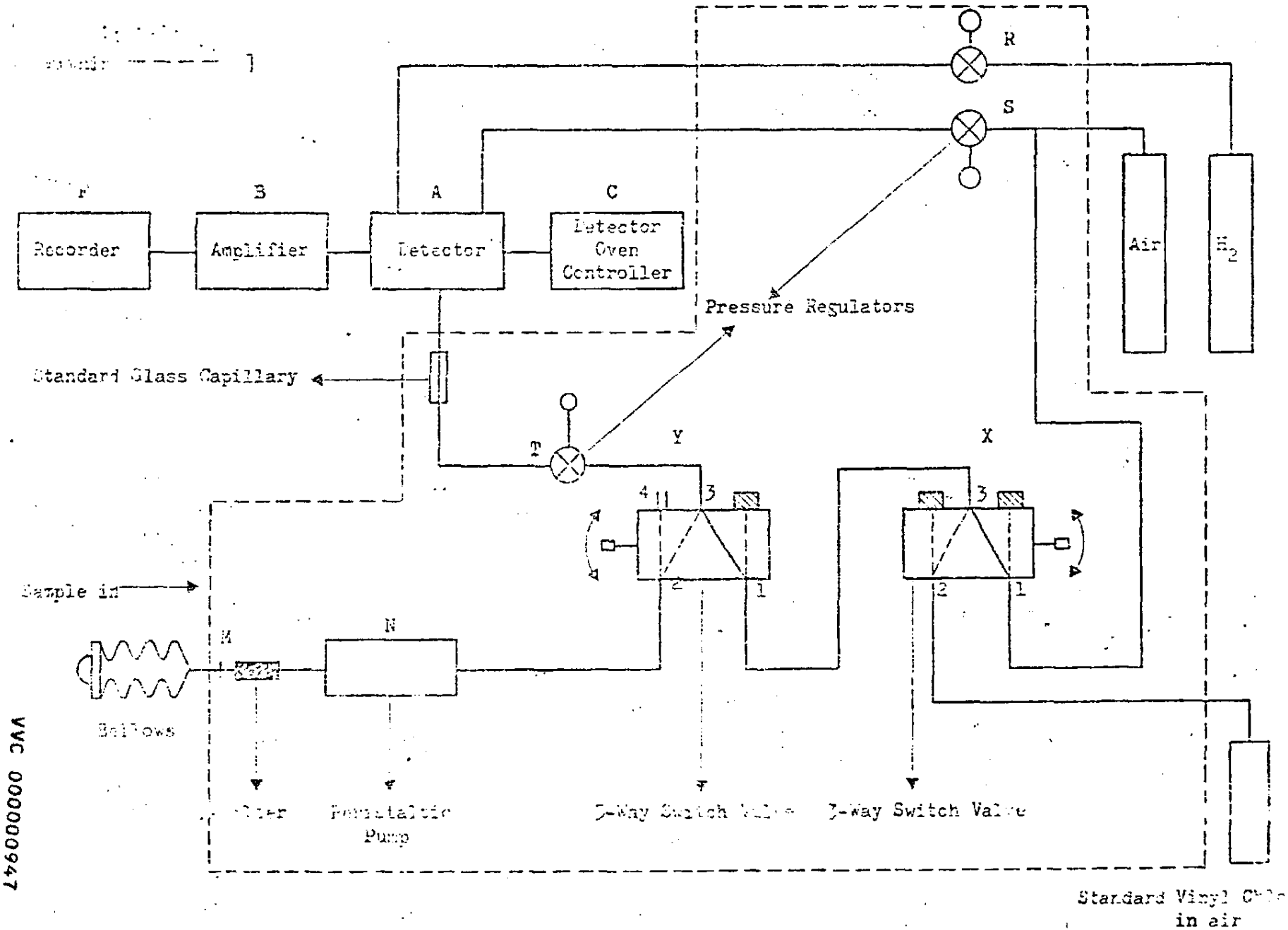
A round bottom flask of known volume, (calibrated using the water method) is evacuated and filled with clean air to atmospheric pressure. A rubber seal of suitable size is inserted into the neck. An aliquot of pure vinyl chloride gas is injected into the flask through the rubber seal using a syringe. The type of syringe used is a 1.0 ml 'Willette Scimitar' disposable syringe. The syringe is flushed out with vinyl chloride gas 6 times before the required volume is measured and injected into the flask. This ensures that

the syringe is saturated with vinyl chloride before the sample is taken. The atmosphere is mixed by piercing the seal with a needle attached to a 10 ml disposable syringe and filling and emptying it into the flask 6 times. One aliquot is injected into the GC apparatus by taking 10 ml and injecting into the evacuated sample loop. Only one aliquot can be taken out of the flask and therefore different atmospheres of the same concentration have to be prepared for duplicate determinations.

Gas Chromatographic Conditions

Detector	Flame ionisation detector
Column	1-metre of silicon elastomer 420 on acid washed 'Celite'.
Column temperature	40°C
Hydrogen flow rate	20 ml/minute
Nitrogen flow rate	30 ml/minute
Air flow rate	500 ml/minute
Sample loop	5 cm^3

The concentration of vinyl chloride is calculated using the peak height method.



VVC 000000947

	1	2	3	4	5	6	7	8	9	10	11	12

STICK ON PARTS LIST - GEN. NOTES / REF. DRGS. TO BE LOCATED ON RH SIDE OF SHEET

COMPONENT LIST

	COMPONENT	SUPP. BY
D1	DIODE S.C.R. 30A PIV 100A	A.E.
PL1	CHASSIS PLUG 4 PIN MK IV	PLESSEY
PL2	CHASSIS PLUG 3 PIN MK IV	PLESSEY
R1	RESISTOR 47Ω 2% CARBON 1W	
R2	RESISTOR 100Ω 2% CARBON 1W	
SCR1	SILICON CONTROLLED RECTIFIER C25/60/B 25A 600V	A.E.
SKT1	FREE SOCKET 4 PIN MK IV	PLESSEY
SKT2	FREE SOCKET 3 PIN MK	PLESSEY

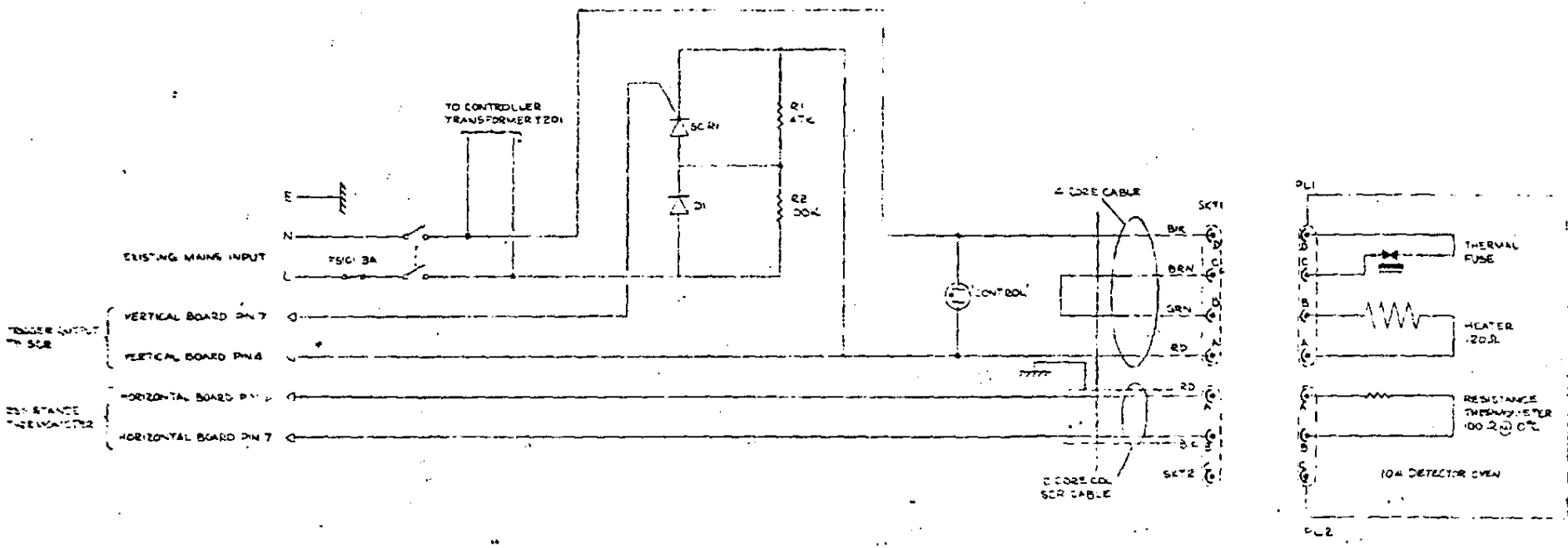


Fig. 2.

VIC 000000948

DRG. No. 09/48

TITLE PYE 104 DETECTOR OVEN CONTROLLER DRIVER UNIT – WIRING DIAGRAM

FACTORY HILLHOUSE

IMPERIAL CHEMICAL INDUSTRIES LIMITED

PLASTICS DIVISION - WELWYN GARDEN CITY

RESEARCH DEPARTMENT

ANALYTICAL DIVISION

THE DETERMINATION OF VINYL CHLORIDE MONOMER IN NON-ALCHOLIC AND ALCOHOLIC DRINKS AND OTHER AQUEOUS SOLUTIONS OR EMULSIONS

INTRODUCTION

The procedures described in this test method are those developed for the determination of low ppm quantities of vinyl chloride monomer leached from PVC bottles into the contained fluids during storage. The method employs a head space sampling gas chromatographic technique, calibrated by the addition of micro-litre quantities of a standardised solution of vinyl chloride in water, to samples of the particular fluid under test which have not been in contact with poly (vinyl chloride).

INSTRUMENTATION

The Perkin Elmer F40 Multifract head space sampling chromatograph is suitable.

Set up the F40 assembly according to the manufacturer's instructions to operate under the conditions given in the table below. Use standard 25 ml capacity F40 sample vials and seals and operate with an equilibration time of at least 3 hours at 30°C before sampling.

Column	4 Metres 1/8" OD S.S. 20% w/w Carbowax 1540 + 0.5% Atpet 80 on silane treated (HMDS) Diatomrite C (60-72 mesh).
Column temperature	45°C
Water bath temperature	30°C
Injector needle temperature	120°C
Injection time	5 sec.
Analysis time	Aqueous solutions (e.g. orange squash) - 10 mins Gin, Vodka - 60 mins Whisky - 90 mins
Purge time	24 sec
Stabilisation time	30 sec
Nitrogen carrier inlet pressure	1.0 Kp/cm^2
Air inlet pressure	1.2 Kp/cm^2

Hydrogen inlet pressure	1.0 Kp/cm^2
Amplifier sensitivity	1 x 1
Recorder (2-pen)	2 mV and 10 or 20 mV. Chart speed 1 cm/min.

An integrator can be used if desired.

PREPARATION OF CALIBRATION SOLUTION

Prepare a saturated solution of vinyl chloride in water at 25°C. by the following method.

Place the bubbler assembly shown in Fig. 1 into a water bath thermostatically controlled at 25°C. Place 70 cm^3 water in the tube and bubble vinyl chloride through the absorber for a minimum period of 2 hours.

Remove 10 cm^3 of this solution into a 125 cm^3 Hypo-vial containing 90.0 cm^3 distilled water. Immediately seal and store this dilute standard solution in a refrigerator at 5°C.

Remove two further 20 cm^3 aliquots of the solution from the bubbler directly into the iodine flasks for standardisation as described below then transfer the remainder of this strong standard solution to a Hypo-vial and immediately seal and store in a refrigerator at 5°C.

STANDARDISATION OF STRONG STANDARD SOLUTION

Solutions Required

Potassium bromide/bromate solution	0.1N
Sodium thiosulphate solution	0.1N (standardised)
Hydrochloric acid solution	Approximately 2N
Potassium iodide solution	20% w/v

Method

Into two 250 cm^3 iodine flasks add 25.0 cm^3 0.1N potassium bromide/bromate solution. Add to each flask 20.0 cm^3 of the saturated vinyl chloride solution from the bubbler and follow this by 15 cm^3 2N hydrochloric acid solution. Immediately stopper the flasks, shake to mix the contents and seal the stopper with a little 20% potassium iodide solution. Allow the flasks to stand in the dark for at least 16 hours. Carefully remove the stopper allowing the potassium iodide to run into the flask, then add a further 10 cm^3 of the potassium iodide solution and titrate the liberated iodine with the 0.1N sodium thiosulphate solution. Carry out a blank on all the reagents used, using 20 cm^3 distilled water instead of the aliquot of sample solution.

Calculation

$$\% \text{ w/v vinyl chloride in solution} = \frac{(\text{Blank titre} - \text{sample titre}) \times 0.003125 \times 100}{}$$

In our experience the value so obtained should be about 0.1% w/v vinyl chloride. The dilute standard solution is labelled at one tenth of this value.

CALIBRATION OF GAS CHROMATOGRAPHIC PROCEDURE

Into a series of 25 cm^3 capacity F40 vials add 5 cm^3 aliquots of the fluid under test which has not been in contact with poly(vinyl chloride). Seal and cap the vials and by means of a Hamilton micro-litre syringe add 0, 2, 5, 10, 20, 30, 70 and 100 μl of the dilute standard vinyl chloride solution. Place the vials in the F40 thermostat bath at 30°C and start the analysis, arranging the minimum 3 hours equilibration before the first standard is sampled by the chromatograph. Measure the peak height of the vinyl chloride peak shown in Fig. 2 for each standard and plot graphs relating peak height to μg vinyl chloride per 5 cm^3 solution. These graphs cover the range 0 - 3 μg and 0 - 15 μg vinyl chloride per 5 cm^3 solution.

EXAMINATION OF SAMPLES

Shake each sample bottle and by means of a pipette transfer 5 cm^3 to a 25 cm^3 capacity F40 vial. Immediately seal and cap the vial and place it in the F40 thermostat bath at 30°C to be processed with a set of calibration standards as described above.

RESULTS

Measure the peak height due to vinyl chloride in the sample chromatogram and by reference to the appropriate calibration graph, calculate the vinyl chloride content of the liquid under test. Report the result as ppm w/v vinyl chloride.

NOTE

Most liquors contain "high boiling" constituents, and it is advisable to process no more than eight samples or standards at any one time. The column temperature should then be raised to about 100°C and allow to purge clear of high boilers. An overnight purge carried out whilst a further set of samples or standards are equilibrating is convenient.

If available, an electronic integrator may be used in conjunction with the chromatograph.

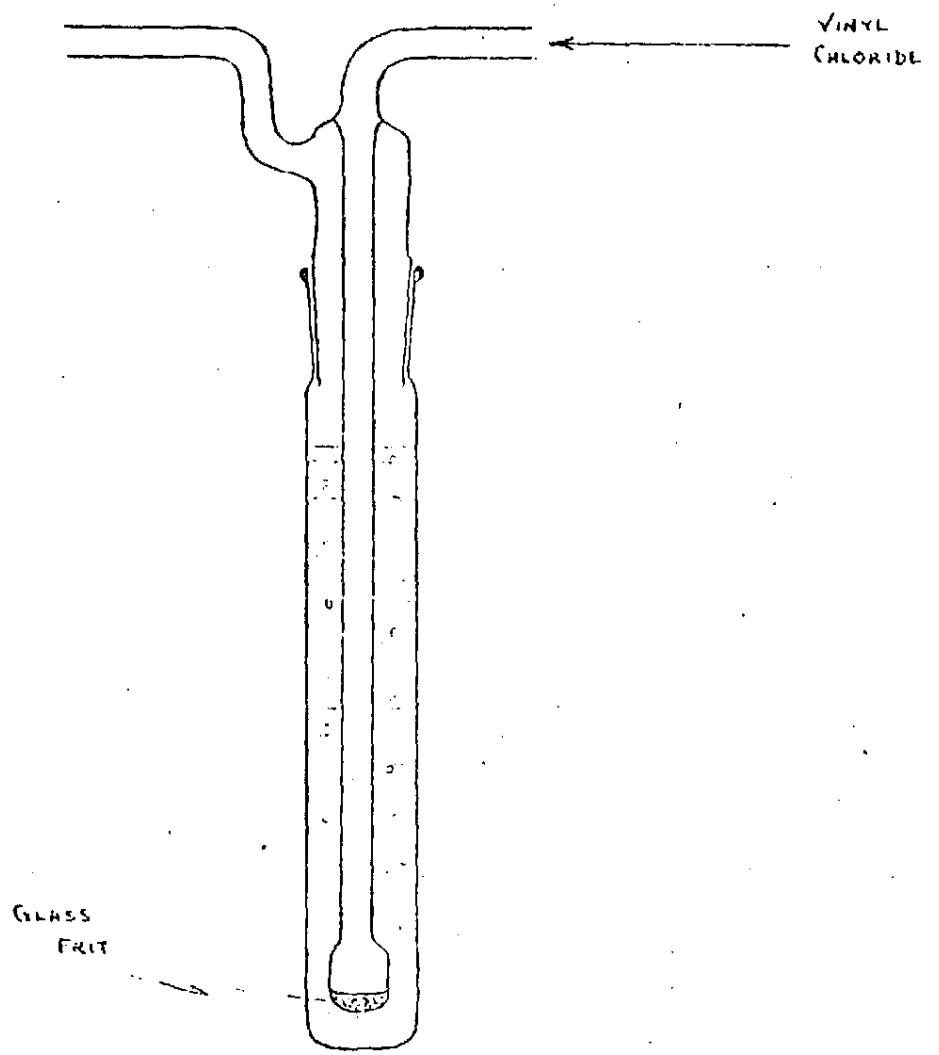
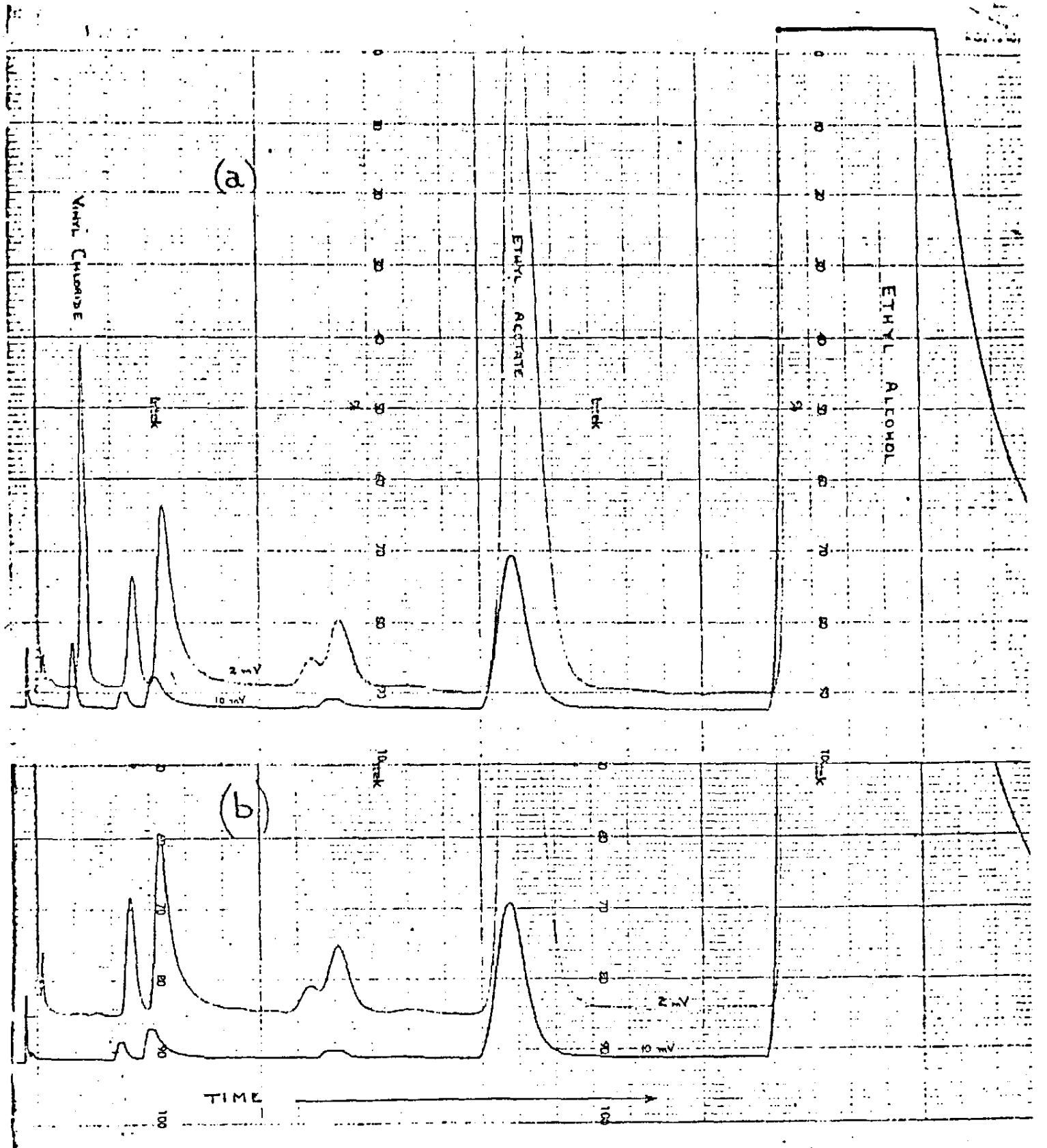


FIG. 1

BUBBLER FOR PRODUCING A SATURATED AQUEOUS SOLUTION OF VINYL CHLORIDE



VVC 000000953

FIG. 2

(a) WM WHISKY from PVC MINATURE BOTTLE - VINYL CHLORIDE CONTENT 0·75 µg or 0·15 ppm v/v

(b) WM WHISKY from GLASS BOTTLE (CONTROL SAMPLE)

IMPERIAL CHEMICAL INDUSTRIES LIMITED
PLASTICS DIVISION - WELWYN GARDEN CITY

RESEARCH DEPARTMENT
ANALYTICAL DIVISION

The Determination of Vinyl Chloride Monomer in Poly (Vinyl Chloride) Powders, Compounds and Mouldings : Headspace Sampling - Gas Chromatographic Method

Analytical Method P73/7

A R Jeffs
N W Wilson

INTRODUCTION

Two methods are used for the determination of vinyl chloride monomer in poly (vinyl chloride) and in both, the analysis is carried out on a solution of the sample in tetrahydrofuran. In the first method, a direct injection procedure is used, whilst in the second, headspace sampling is employed. The latter procedure, described here, is particularly preferred for samples containing less than 200 ppm vinyl chloride monomer and has a lower limit of detection of 0.5 ppm. Although the use of an automatic headspace sampling chromatograph is specified in this method, the procedure can be modified to use simpler equipment with manual headspace sampling by means of a gas tight syringe into a standard chromatograph.

APPARATUS

Headspace sampling gas chromatograph	The Perkin Elmer F40 Multifract instrument is suitable.
Sample vials and seals	25 cm^3 F40 vials are suitable.
Magnetic stirrer	
Volumetric flasks	25 cm^3 and 10 cm^3.
Hamilton syringe	10 µl.
Micrometer syringe	0.5 cm^3. An Agla syringe is suitable.

REAGENTS

PVC homopolymer powder (Monomer free)	Store PVC homopolymer powder in a well ventilated situation until all residual monomer has volatilised. Polymer containing less than 0.5 ppm as determined by this test method is required.
Tetrahydrofuran	This solvent may contain both high boiling impurities which will prolong the analysis and low boiling constituents which will interfere with the determination of vinyl chloride particularly at low concentrations. Remove such impurities by refluxing the solvent over potassium hydroxide and careful distillation with rejection of the foreruns.

Vinyl chloride	Cylinder containing liquid monomer.

GAS CHROMATOGRAPHIC CONDITIONS

Set up the F40 chromatograph according to the manufacturer's instructions to operate under the conditions given in the table below. Use standard 25 cm^3 capacity F40 sample vials and seals and operate with an equilibration time of at least 3 hours at 30°C before sampling.

Column standard	4.00 metres 1/8", OD S/S packed with 20% w/w 'Carbowax' 1540 + 0.5% w/w 'Atpet' 80 on silane (HMDS) treated 'Diatomite' C (60-72 mesh).
Column temperature	45°C.
Water bath temperature	30.0°C.
Injector needle temperature	120°C
Injection time	5 sec.
Analysis time	30 min. (This time will vary with the purity of the tetrahydrofuran solvent and the level of monomer content being determined i.e. the amplifier setting and millivolt range of the recorder used).
Purge time	24 sec.
Stabilisation time	30 sec.
Nitrogen carrier inlet pressure	1.0 Kp/cm^2.
Hydrogen inlet pressure	1.0 Kp/cm^2.
Air inlet pressure	1.2 Kp/cm^2.
Amplifier sensitivity	1 x 1.
Recorder	Servoscribe (2-pen). The mV ranges used depend on the level of monomer content determined i.e. 0.66 mV and 5 mV respectively are used for 0.2-8 µg. 2 mV and 20 mV respectively are used for 5-30 µg. 20 mV and 100 mV respectively are used for 30-500 µg. Chart speed 1 cm/min.

CALIBRATION : HIGH RANGE : 0 - 400 µg VINYL CHLORIDE

Accurately weigh a 25 cm^3 volumetric flask containing approximately 20 cm^3 redistilled tetrahydrofuran. Add about 1 g vinyl chloride liquid and

quickly stopper and reweigh the flask. Make the volume up to the mark with redistilled tetrahydrofuran, mix and store in a refrigerator. Calculate the exact strength of this standard vinyl chloride solution.

Weigh 0.500 g ± 1 mg portions of monomer-free polymer into a series of 25 cm capacity F40 vials. Add 5.0 cm^3 redistilled tetrahydrofuran and immediately seal and cap the vials. Allow the polymer to dissolve.

The addition of tetrahydrofuran to the polymer powder can cause gelation so that complete solution takes several hours, even with mechanical shaking. Solution within a few minutes can be obtained by use of a magnetic stirrer. The F40 vial containing the polymer and magnetic bar are placed on the stirrer and 5.0 cm^3 of tetrahydrofuran added rapidly from a syringe or dispenser. Small stirrer bars are conveniently made from short lengths of steel wire, sealed into glass melting point tubing.

When the solutions are ready, by means of a 10 µl Hamilton syringe add, through the caps of separate vials 0, 1, 3, 7 and 10 µl aliquots of the standard vinyl chloride solution to give a range of standards, which when prepared from a starting 4% solution, cover the range 0-400 µg vinyl chloride.

Place the prepared vials together with any sample vials in the F40 thermostat bath at 30°C and after allowing a minimum equilibration period of 3 hours start the automatic analysis sequence. On each chromatogram measure the height of the peak due to vinyl chloride and plot a graph relating peak height to µg vinyl chloride per vial.

CALIBRATION : LOW RANGE : 0 - 20 µg VINYL CHLORIDE

By means of a micrometer syringe transfer 0.500 cm^3 of the standard vinyl chloride solution, prepared for the high-range calibration, to a 10 cm^3 volumetric flask containing a little redistilled tetrahydrofuran. Dilute to the mark with redistilled tetrahydrofuran, mix and store in a refrigerator. Calculate the exact strength of this dilute standard vinyl chloride solution.

Using this solution carry out the procedure described for the high range calibration. When prepared from a dilute standard solution containing 0.2% vinyl chloride these standards cover the range 0-20 µg monomer.

EXAMINATION OF SAMPLES

Powder samples should be stored in tightly sealed containers whilst awaiting analysis. As quickly as possible, weigh 0.500 g ± 1 mg of the sample into an F40 vial. Add 5.0 cm^3 redistilled tetrahydrofuran and immediately seal and cap the vial. Dissolve the polymer as described for the high range calibration, and when solution is complete transfer the vial together with the standards to the F40 thermostat bath to complete the analysis. Measure the peak height due to vinyl chloride on the chromatogram produced.

RESULTS

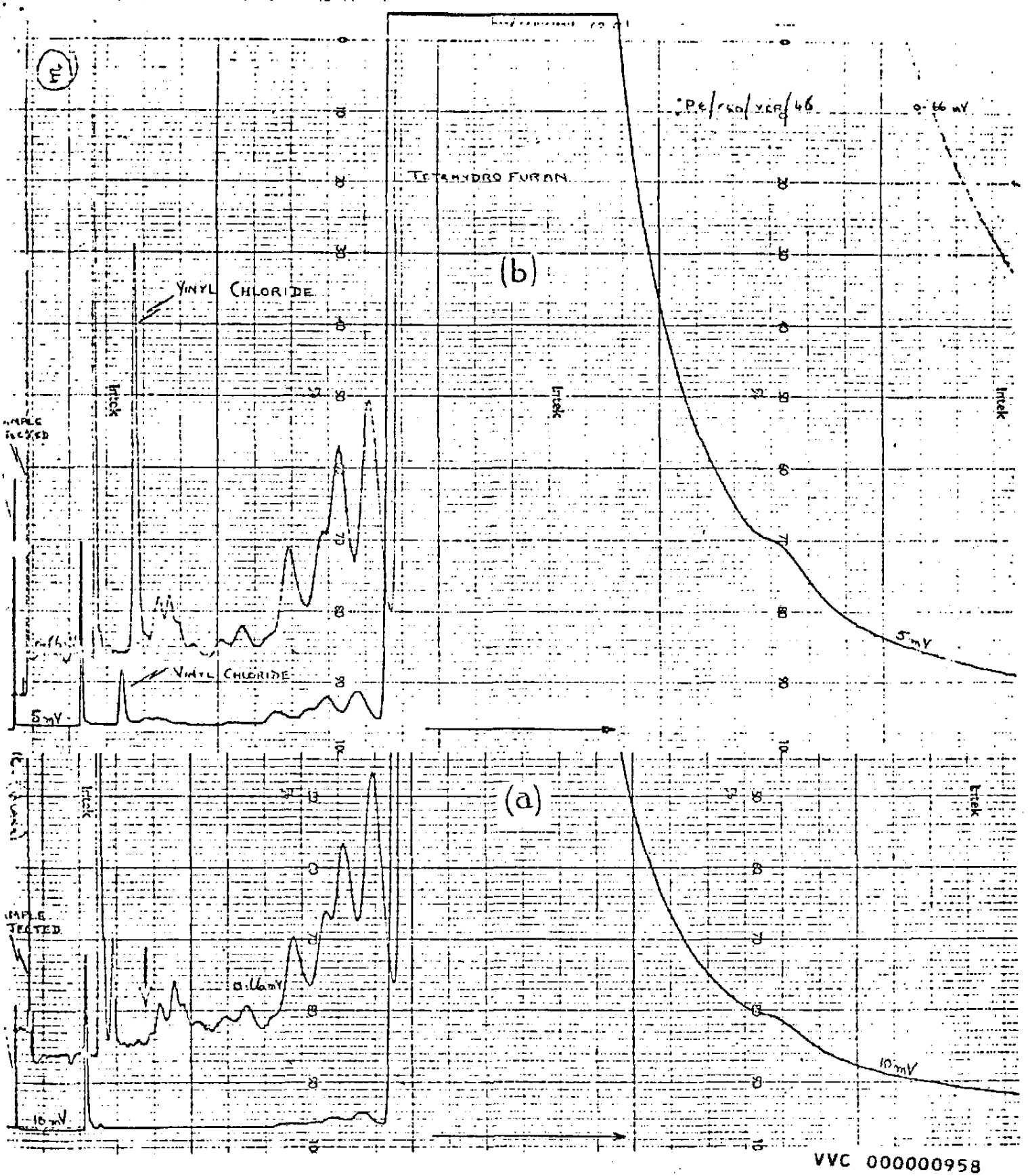
Refer the peak height due to vinyl chloride in the sample chromatogram to the appropriate calibration graph and hence calculate the vinyl chloride content of the sample. Report the result as ppm w/w vinyl chloride.

NOTES

If available, an electronic integrator may be used in conjunction with the chromatograph.

It is often convenient to purge the chromatographic column free of accumulated high boiling constituents by increasing the column temperature to 100°C overnight. During this time a further set of samples and/or standards can be equilibrating in the 30°C thermostat bath.

Typical chromatograms are shown in the figure.



VVC 000000958

(a) Headspace Chromatogram from Sample containing no Vinyl Chloride (Solvent impurities only)

(b) Headspace Chromatogram from Sample of PVC compound containing 8·1 ppm v/v Vinyl Chloride