Inter-office memo

TENNECO CHEMICALS, INC.

To H. B. Carr At Burlington Date March 31, 1969

From F. W. Kanzler At Burlington Copy to

Subject Technical Memorandum
Gas Chromatographic Determination of
Impurities in Vinyl Chloride Monomer

CONCLUSIONS:

1. A gas chromatographic method has been developed for the analysis of light end impurities in both virgin and recovered vinyl chloride monomer.

2. The analysis is accomplished by syringe injecting a gas sample from the headspace of a sample bomb into a F & M 5754A gas chromatograph equipped with a Tributyl Phosphate column and a hydrogen flame ionization detector. A detailed outline of the analysis is described in B.A.C.M. #1 which is attached as Figure 1.

3. The sensitivity of this method is to less than one part per million.

4. Preliminary studies indicate that the method provides good correlation with other laboratories (Table 1).

5. The time required for the analysis is approximately one hour.

RECOMMENDATIONS:

1. The method should be further developed to provide capability for the analysis of heavy end impurities in MVC.

2. The correlation studies should be continued.

3. The gas sampling valve on the F & M 5754A should be modified for use with MVC in order to provide a more rapid and reproducible method of injecting the gas phase sample.

DISCUSSION:

1. Column Selection

A literature search provided information about several liquid phases and solid supports used for MVC or related analyses. These were:

Liquid Phase	Solid Support
Silicone Gum Rubber	Anakrom ABS
B,B' - Oxidipropionitrile	Chromosorb W/AW
Diethylene Glycol Succinate	Chromosorb W/AW
Tricresyl Phosphate	Chromosorb P/AW and W/AW
Tributyl Phosphate	Chromosorb P/AW

It was decided to use a Tributyl Phosphate liquid phase on Chromosorb P/AW solid support, as it offers excellent separation of the following light end impurities:

Ethane
Ethylene
Propane
Propylene
Acetylene
Isobutane
Allene (Propadiene)
Butane
Butene-1
Methyl Acetylene
Methyl Chloride
Butene-2, trans and cis
1,3 Butadiene

Houston also uses this column. However, a 30% liquid phase of Tributyl Phosphate on Chromosorb P as used in Houston seems to be somewhat high, for a "conditioning" of the column was observed over a period of almost two weeks.

For anticipated future heavy ends analysis the higher boiling Tricresyl Phosphate liquid phase may be superior to Tributyl Phosphate as it permits analysis at higher oven temperatures.

It is of interest to note that of the three solid supports checked, only Chromosorb P/AW would render a good separation. This is probably due to the relatively large

surface area (4.0 m^2/g for Chromosorb P versus 1.0 m^2/g for Chromosorb W) and to the smaller porosity (1.1 cc/g for Chromosorb P and 2.8 cc/g for Chromosorb W).[1]

2. Operating Parameters

Column: 12' x 1/4" SS 20% Tributyl Phosphate on Chromosorb P/AW 60 - 80 mesh
Carrier Gas: Helium, at a flow rate of 47 cc/min. with a column "in" pressure of 50 psig and a column "out" pressure of 14.7 psia
Hydrogen: 60 cc/min. flow, 40 psig line pressure
Air: 350 cc/min. flow, 20 psig line pressure
Oven Temperature: Ambient (about 25°C)
Injection Port Temperature: 130°C
Detector Temperature: 260°C

3. Identification of Impurities

The identification of the impurities was arrived at by:

a. Injection of pure gases and subsequent identification of the sample impurities by matching the retention times of the various gases.
b. "Spiking" of samples with pure contaminants and comparing the peak intensities of the "spiked" with the "un-spiked" sample.

4. Contamination Sources

Difficulties were encountered on initial routine analysis by the occurrence of a very high level "background" contamination after the elution of the vinyl chloride. This contamination resulted in an extreme loss of sensitivity for low level (< 25 ppm) impurity analyses. At this stage of the method development a "Push-Pull" gas inject valve was used to introduce the sample onto the column. To find the source of contamination the following steps were undertaken:

a. Column "Bleeding" - A check on column bleeding was negative.
b. Detector - Upon dismantling of the detector assembly it was found that the copper alloy solder of the detector jet exhibited a high degree of corrosion. A new set of detector jets was secured and installed but resulted in the same background contamination. To eliminate the corrosion problem, caused mainly by the eluting MVC, a threeway ball valve was in-

[1] A. M. Filbert, M. L. Hair, J. of Chromat. Science, Vol. 7, February, 1969.

stalled at the exit of the column before the detector. This allows the detector to be by-passed during the elution of the vinyl chloride and has reduced the corrosion. Hewlett and Packard has been notified of this problem and is investigating the use of more inert detector jet solder.

c. Gas Inject Valve - The gas inject valve was by-passed by injecting a sample with a gas syringe directly onto the column. This step resulted in an elimination of the background contamination. The cause was traced to an interaction of the MVC with six silicone rubber O-rings which seal the various chambers of the gas inject valve. Since the use of the gas inject valve offers the best assurance of reproducible injects, more inert Viton O-rings were installed. Again, the result was contamination. Hewlett and Packard was contacted and after a visit to their laboratories, they have agreed to supply us with a Teflon lined gas inject valve, which has shown no contamination during repeated MVC injects.

5. Calibration and Sampling

Owing to the difficulty of finding a suitable internal standard, calibrated MVC standards are used for the quantitative determination of the impurities.

Until the installation of the Teflon gas inject valve, syringe injection will be used for this analysis. The calibration and analysis is carried out by transferring a calibration gas or sample gas to a special manufactured "Glass Bag". The sample is transferred from the sample bomb to the glass bag and subsequently withdrawn with a syringe through a serum stopper contained on the glass bag. The sample size of 2.5 ml was found to yield reproducible results. Due to the excellent peak resolution the calculation is based on the peak height. A typical chromatogram is shown in Figure 4 of the attached B.A.C.M. #1.

Fred W. Kanzler

FWK/rjl

TABLE 1

CORRELATION BURLINGTON VS. HOUSTON

Component	83486 Burl	83486 Houston	38048* Burl	38048* Houston	83011 Burl	83011 Houston	38047 Burl	38047 Houston	Allied 714601 Burl	Allied 714601 Houston	PPG 9902 Burl	PPG 9902 Houston
	PPM		PPM		PPM		PPM		PPM		PPM	
Propane	8	4	1	11			8	7	<1	0.2	ND	ND
Propylene	11	6	3	3			10	7	4	2	ND	0.1
Isobutane	5	5	4	9			Not Calc	1	<1	0.5	<1	ND
Allene	101	88	87	115	50	46	15	18	<1	0.4	<1	0.1
Butane	6	3	6	12			2	3	<1	1	<1	ND
Butene-1	4	4	6	2			3	6	<1	0.7	<1	0.1
Methyl Acetylene	41	42	56	19	26	26	6	12	<1	ND	<1	ND
Methyl Chloride	ND	ND	<1	ND			<1	Tr	149	150	50	52
Cis-Butene-2	ND	ND	<1	ND			<1	-	ND	-	ND	-
1,3 Butadiene	2	1.2	17	3			4	1	2	1	6	5

*In future cases, such as this, Houston will be notified and a sample will be sent to them for repeat analysis.

LABORATORY WORK SCHEDULE

Date	Ken	John	Dick	Bob	Mark	Roger	Al	Harold
10/13	12-8	12-8	4-12	4-12	8-4	8-4	Off	Off
14	12-8	12-8	Off	Off	8-4	8-4	4-12	4-12
15	12-8	12-8	Off	Off	8-4	8-4	4-12	4-12
16	12-8	12-8	8-4	8-4	Off	Off	4-12	4-12
17	12-8	12-8	8-4	8-4	Off	Off	4-12	4-12
18	Off	Off	8-4	8-4	12-8	12-8	4-12	4-12
19	Off	Off	8-4	8-4	12-8	12-8	4-12	4-12
20	Off	Off	8-4	8-4	12-8	12-8	4-12	4-12
21	4-12	4-12	8-4	8-4	12-8	12-8	Off	Off
22	4-12	4-12	8-4	8-4	12-8	12-8	Off	Off
23	4-12	4-12	Off	Off	12-8	12-8	8-4	8-4
24	4-12	4-12	Off	Off	12-8	12-8	8-4	8-4
25	4-12	4-12	12-8	12-8	Off	Off	8-4	8-4
26	4-12	4-12	12-8	12-8	Off	Off	8-4	8-4
27	4-12	4-12	12-8	12-8	Off	Off	8-4	8-4
28	Off	Off	12-8	12-8	4-12	4-12	8-4	8-4
29	Off	Off	12-8	12-8	4-12	4-12	8-4	8-4
30	8-4	8-4	12-8	12-8	4-12	4-12	Off	Off
31	8-4	8-4	Off	Off	4-12	4-12	12-8	12-8
11/1	8-4	8-4	Off	Off	4-12	4-12	12-8	12-8
2	8-4	8-4	Off	Off	4-12	4-12	12-8	12-8
3	8-4	8-4	Off	Off	4-12	4-12	12-8	12-8
4	8-4	8-4	4-12	4-12	Off	Off	12-8	12-8
5	8-4	8-4	4-12	4-12	Off	Off	12-8	12-8
6	Off	Off	4-12	4-12	8-4	8-4	12-8	12-8
7	Off	Off	4-12	4-12	8-4	8-4	12-8	12-8
8	12-8	12-8	4-12	4-12	8-4	8-4	Off	Off
9	12-8	12-8	4-12	4-12	8-4	8-4	Off	Off
10	12-8	12-8	4-12	4-12	8-4	8-4	Off	Off
11	12-8	12-8	Off	Off	8-4	8-4	4-12	4-12
12	12-8	12-8	Off	Off	8-4	8-4	4-12	4-12
13	12-8	12-8	8-4	8-4	Off	Off	4-12	4-12
14	12-8	12-8	8-4	8-4	Off	Off	4-12	4-12
15	Off	Off	8-4	8-4	12-8	12-8	4-12	4-12
16	Off	Off	8-4	8-4	12-8	12-8	4-12	4-12
17	Off	Off	8-4	8-4	12-8	12-8	4-12	4-12
18	4-12	4-12	8-4	8-4	12-8	12-8	Off	Off
19	4-12	4-12	8-4	8-4	12-8	12-8	Off	Off
20	4-12	4-12	Off	Off	12-8	12-8	8-4	8-4
21	4-12	4-12	Off	Off	12-8	12-8	8-4	8-4
22	4-12	4-12	12-8	12-8	Off	Off	8-4	8-4
23	4-12	4-12	12-8	12-8	Off	Off	8-4	8-4
24	4-12	4-12	12-8	12-8	Off	Off	8-4	8-4
25	Off	Off	12-8	12-8	4-12	4-12	8-4	8-4
26	Off	Off	12-8	12-8	4-12	4-12	8-4	8-4
27	8-4	8-4	12-8	12-8	4-12	4-12	Off	Off
28	8-4	8-4	12-8	12-8	4-12	4-12	Off	Off
29	8-4	8-4	Off	Off	4-12	4-12	12-8	12-8
30	8-4	8-4	Off	Off	4-12	4-12	12-8	12-8
12/1	8-4	8-4	Off	Off	4-12	4-12	12-8	12-8
2	8-4	8-4	4-12	4-12	Off	Off	12-8	12-8