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THE EVALUATION OF TWO NEW METHODS FOR
MEASURING RESIDUAL VINYL CHLORIDE IN GEON RESINS

By

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Summary:

The head space method of analysis for residual vinyl chloride monomer is a viable method of analysis for residual vinyl chloride in Geon resins. The work done in evaluating this method has shown it to be much more reproducible than the solvent method now being used by Goodrich production plants. Data indicates the head space method of analysis will give reproducible results with a deviation of 20% within the broad range covered by this analysis. (1 to 2000 PPM vinyl chloride) The head space method has the advantage of being a faster and cleaner analysis than the solvent method now being used. The head space analysis is more sensitive than the solvent method. This method of analysis has given good results in the low parts per million range (1. to .5 PPM) and should be usable into the high parts per billion range.

The head space method of analysis is upset by other low boil materials when present in the samples being analyzed. These materials will disrupt the equilibrium in the head space introducing an error in the results. The extent of this error has not yet been fully investigated.

The direct method of analysis, although not as fast as the head space method, is faster than the solvent method. This is due to the sample preparation requiring from $\frac{1}{4}$ to $1\frac{1}{2}$ hours for the solvent method compared to 2 to 3 minutes for the direct method. The direct method of analysis is not as sensitive as the head space method due to the smaller sample used for analysis. However, it is more sensitive than the solvent method currently in use. The direct method of analysis has the advantage of giving much better separation of all the components coming from a sample being analyzed. This is due to the temperature programming of the chromatograph during the analysis.

The drawback to the direct method of analysis is the operation of the chromatograph. The procedure for this analysis requires the chromatograph column to be cooled before the analysis is started.

A comparison of the head space method (an equilibrium system) with the direct method (a non-equilibrium system) as applied to the analysis of Geon 103EP76 shows excellent agreement. This is a strong indication but not absolute proof that these two methods are accurate from a standpoint of absoluteness.

Work done in this investigation has shown that more work is needed to perfect any of the three methods of analysis for residual vinyl chloride. All three analyses are based on gas chromatograph evaluations. The gas chromatograph is mainly a quantitative instrument and it is very important to know the composition of the samples being analyzed. The composition of our many Geon resins vary greatly and without a thorough investigation of each resin there is reason to doubt the data generated from any analysis due to interferences from other materials eluting along with the vinyl chloride.

Conclusions:

1. The test method proposed by A. Berens is a faster analysis than the solvent method now being used by BFG Production Plants. An analysis can be run every four (4) minutes with this method, compared to fifteen minutes needed for the solvent method.

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2. The head space analysis is cleaner than the solvent method in that no back flushing is needed to eliminate solvents and also there is no contamination from solvent impurities.
3. The head space analysis has shown good reproducibility both at the Technical Center and at Avon Lake General Chemical plant. There is also a good correlation of results between the Technical Center and General Chemical.
4. The simplicity of the head space analysis allows the testing laboratory to give analytical results of a sample twenty-five minutes after receiving the sample compared to one hour to one and a half hours for the solvent method.
5. Because of the large sample size (1.0 to 0.3 cc) used in the head space analysis, it should give greater accuracy in the low parts per million range than the solvent system.
6. There is good agreement between the head space method and the direct method of analysis in the few cross checks run.
7. The direct method gives better separation of the volatiles in a resin sample. This separation allows a more accurate measurement of the residual vinyl chloride peak. Data indicates there is some interference in the solvent method of analysis due to other volatile components in 80X5 resin. This interference causes the analysis to give a higher level of residual vinyl chloride than is actually present in the sample.

Future Course of Action:

1. An investigation is currently underway to investigate the degree of error introduced into the head space analysis due to other low boil components in the head space of the sample vial. Beyond this, no further work is planned.

Recommendations

- 1) Experiments should be designed to test the absoluteness of the three methods.

Introduction

Two new test methods have been developed for the determination of residual vinylchloride in Geon resins. This report covers the work in developing these methods and applying them to actual analyses.

The first method, proposed by A. R. Berens, is based on the residual vinyl chloride in a resin reaching an equilibrium in a closed container. This equilibrium distributes the vinyl chloride between the resin sample and the head space gas of the container. The vinyl chloride equilibrates very rapidly when the

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sample is heated above the glass transition temperature of the resin. The analysis is conducted by sampling the head space gas of the sealed container and calculating the vinyl chloride in the head space, knowing the equilibrium conditions the residual vinyl chloride in the resin can then be calculated from this head space analysis. This method is very clean compared to the solvent method now being used in BFG production plants. That is to say, there are no interferences from solvents or contaminants from solvents. Work at the Avon Lake Technical Center and the Avon Lake General Chemical Plant has shown this analysis to be practical for production plant use.

The second method is a more direct analysis. A small sample of resin to be analyzed is weighed into a glass tube. This tube is inserted directly into the injection port of a 5710 Hewlett-Packard gas chromatograph for analysis. The heat of the injection port drives off the residual vinyl chloride and the chromatograph carrier gas sweeps it into the column for analysis. This method has not yet been tried in any production plant, however, data generated at the Technical Center shows it to be a viable method for residual vinyl chloride analysis. This method of analysis can also be used for residual vinyl chloride in Geon compounds. It will also detect other components such as vinyl acetate or vinylidene from copolymers. These two new methods for analysis of residual vinyl chloride were suggested separately, the vapor space analysis by Berens of the Research Center and the direct method by myself at the Technical Center. We had started an evaluation of the direct method of analysis at the Technical Center, prior to hearing A. Berens' vapor space analysis. In a meeting with A. Berens' it was decided a more meaningful evaluation of these two methods would be obtained if both methods were evaluated together. In this way data would be generated which could be used to directly compare the two methods. (At that time no data had been generated using the head space analysis.) We could not include the solvent method in this evaluation as we did not have the backflushing equipment required for this analysis. A few comparisons of the three methods have been made, using the Avon Lake General Chemical Plant's equipment.

In all of the work done on the two analyses, no attempt has been made to optimize the conditions for running either test. We have only established test conditions which give benchmark for the evaluation of the two methods. I am referring here to chromatograph conditions such as flow rate of the carrier gas temperatures (column, injection port, and detector), column packing and column length. All of these parameters will influence the ability to detect vinyl chloride and separate it from other volatile materials used in the manufacturing of polyvinyl chloride resins.

At first glance, this does not seem important, however, data presented below will show that good separation of residual vinyl chloride from other polymerization materials does become important when measuring in the low parts per million range. It must also be pointed out that no attempt has been made to establish the absolute-ness of either test. The vapor space method relies on an equilibrium being established in the sample vial. Then from an equilibrium constant the total residual vinyl chloride in the sample is calculated from the vinyl chloride analyzed in the head space of the vial. To verify that the level of residual vinyl chloride found in this manner is indeed real, a sample of resin with a known level of vinyl chloride is needed as a control. No such sample is available.

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In the direct method of analysis, a sample of resin is heated inside of the gas chromatograph in an effort to drive off all of the residual vinyl chloride monomer from the sample. With this method there is a question about any vinyl chloride being left in the sample. In an attempt to determine this, samples have been rerun using this method to see if any more vinyl chloride could be driven off. To date we have not been able to detect any monomer coming off of the sample which had been previously tested. When a sample resin is run using both methods of analysis, very good agreement is evident between the two independent sets of data.

It is known that vinyl chloride has poor sensitivity in a flame ionization detector (FID). That is, the detector response for vinyl chloride is much lower than for most hydrocarbons. This is probably due to the stability of the vinyl chloride molecule which in turn does not yield a high concentration of charged particles in the FID detector.

The vapor space and the direct method of analysis overcome this problem by putting more vinyl chloride into the detector and thereby increasing the sensitivity of the two methods well above the solvent method. This increase in sensitivity is about two to three thousand times greater than the solvent method due only to the increase in sample size. For example, a resin containing 100 ppm residual vinyl chloride, analyzed by the solvent method would put approximately 1.5 nanograms of vinyl chloride on the chromatograph detector. This same resin sample analyzed by the vapor space method would put approximately 4,000 nanograms of vinyl chloride on the chromatograph detector.

By the direct method of analysis the detector would see 2,000 nanograms of vinyl chloride. These figures are based on a 30 microliter sample of 5% resin/solvent solution for the solvent method; 0.3 cc air sample taken over a two gram resin sample for the vapor space analysis, and a 20 milligram resin sample using the direct method of analysis.

With this increased test sensitivity, it should now be possible to look at residual vinyl chloride monomer in the parts per billion range. It also allows the use of a gas chromatograph with a thermocouple detector (TC) to be used for residual vinyl chloride analysis. If this type of detector (TC) were used it would not be necessary to calibrate the chromatograph each day as air (not detected with FID) could now be used as an internal standard. No work has been done with a TC detector here at the Technical Center as we do not have a chromatograph with a TC detector available to us. Berens has done work with this type of instrument and demonstrated the feasibility of it.

There are some problems with these two new methods of analysis which must be mentioned. In the vapor space analysis interference from other low boil materials used in polymerization will disrupt the vapor space equilibrium. This disruption will cause the analytical results to be lower than the actual residual vinyl chloride in the resin. This problem can easily be spotted during the analysis by the appearance of other peaks in the chromatogram. Low boil materials are not common in most Geon resins and therefore this problem does not put much restriction on this method.

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The problem with the direct method of analysis is one of chromatograph operation. When the resin sample is inserted into the injection port of the chromatograph there is not an instantaneous release of all the residual vinyl chloride. Actually, the vinyl chloride is released over a period of time determined by the temperature of the injection port and the length of time it takes the resin to reach this temperature. To compensate for this time dependent release of all of the vinyl chloride, a small section of the chromatograph column is frozen with dry ice prior to introducing the sample. This allows for a collection of the vinyl chloride at the frozen section of the column, and then as heat is applied to the column during the course of the analysis a plug type flow of the vinyl chloride is achieved which then gives a sharper chromatogram peak. This allows for a more accurate measurement to be made.

Experimental Results

Head Space Method

(1) Response Factor for Vinyl Chloride:

Preliminary work in developing the vapor space analysis was started by determining a response factor for vinyl chloride on the Hewlett-Packard 5710 gas chromatograph. This was done using mixtures of vinyl chloride gas and air. Calibration gas at 19 ppm vinyl chloride in air was purchased and other concentrations were made up at the Technical Center from compressed air and a 1% mixture of vinyl chloride in air. (1) Response factors determined from the calibration gas mixtures are based on the chromatograph peak area per nanogram of vinyl chloride. Nanograms of vinyl chloride per cc of calibration gas were calculated using the method described in the Appendix (1).

Table #1 is a tabulation of the VCM response factors obtained for the calibration gas mixtures.

The data in Table 1 indicate a change in the response factor for low concentrations of vinyl chloride. It appears that the detector response increases as the vinyl chloride concentration decreases. However, the calibrating gas used for the first 8 determinations is different from that used for the remaining runs. The first eight data points represent a premixed sample of vinyl chloride and air which was purchased rather than mixed at the Technical Center as the other samples were. An error in our calibration gas could be causing this difference in response.

- (1) George Leas prepared all of the calibration gas mixtures used in our work. His method for making the different concentrations is reported by M. O'Mara Feb. 28, 1974 - Analytical system for measuring the adsorption of VCM on charcoal.

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At this point it was felt we could determine what was happening in this low nanogram range by running another calibration curve mixing low parts per million vinyl chloride and air using the same technique as used for the higher concentrations. Prior to doing this we would keep with in our experimental plan and run some resin samples using the average response factor found in Table 1 (2.4) to see how well the head space analysis would reproduce.

A sample of Geon 103EPT-76 was obtained from Avon Lake General Chemical Plant. This resin sample was run seven times using the head space analysis. The residual vinyl chloride monomer was calculated for each run using the average response factor obtained from Table 1. Table 2 is a tabulation of the data obtained from this experiment. These data shows the test to give very reproducible results for this sample of resin. The spread of results is only 4 ppm and the maximum deviation from the average results is 2.6 ppm. Comparing these data with some results obtained by the solvent method, the vapor space method looks very good. For example, a sample of 110X334 resin was run by the solvent method 9 times. The spread of the test results was 34 ppm, (from 3 ppm to 37 ppm) and the maximum deviation from an average was 24 ppm. The resin tested here was also in the range of 30 ppm residual vinyl chloride.⁽²⁾

At this point our work was interrupted due to the loss of the chromatograph in the Mass Spectrometry Lab. We were given another Hewlett-Packard 5710 instrument to use for several days. This instrument was located in the pollution lab at the Technical Center. When we set this instrument up for the vapor space analysis, it was noted that there was a two fold increase in response to vinyl chloride, compared to the response on the instrument in the Mass Spec Lab. Investigation of this showed that water in the air supply to the detector was suppressing the response of the Mass Spectrometry instrument. This problem with the instrument in the Mass Spec. Lab was corrected by switching the air supply from plant air to compressed air from a cylinder.

Using the instrument in the pollution lab we again began our work by running calibration gas mixtures to establish a response factor for this instrument. In an attempt to define the change in response at low concentrations of vinyl chloride, (See Table 1) we ran samples of calibration gas at 5 ppm vinyl chloride prepared at the Technical Center. By using different volumes of this 5 ppm sample and the independently prepared standard (19 ppm vinyl chloride) we would get an overlap of data. If the data showed difference in response between these chromatograph runs, it would indicate we had an error in one of the calibration gases. If both calibration gases showed a high response in the low nanogram range it would now indicate the response to vinyl chloride was not linear in the low nanogram area.

(2) Data presented by R.S. Morgan in his letter to E.G. DeCapita 3/19/74.

Table 2

Head Space Analysis of 103KPP-76 - Reproducibility Test

<u>GC Run Number</u>	<u>Sample Identification</u>	<u>Sample Weight (gms)</u>	<u>G.C. Sample Size (cc)</u>	<u>GC Peak Area</u>	<u>Response Factor</u>	<u>Residual VC1 (ppm)</u>
3-30-74-7	103KPP-76 Bin #1 1513 hrs.	1.81941	.3	2624	2.4	30
3-30-74-8	" " "	1.80302	.3	2720	2.4	31
3-31-74-13	" " "	1.83742	.3	2688	2.4	31
3-31-74-14	" " "	1.70644	.3	2416	2.4	29
3-31-74-15	" " "	1.95194	.3	2736	2.4	30
3-31-74-16	" " "	1.89607	.3	2576	2.4	29
3-31-74-17	" " "	1.94078	.3	2434	2.4	27

Average residual VC1 29.6
Maximum deviation from average 2.6

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It was also decided to expand the calibration curve to higher levels of vinyl chloride. To do this a calibration gas mixed at the Technical Center at 2,000 PPM vinyl chloride was included in this experiment.

The data generated in this experiment are tabulated in Table #3. These data represent sixty eight (68) chromatograph runs using five (5) different concentrations of vinyl chloride in air. By charging different amounts of each vinyl chloride concentration to the chromatograph, seventeen (17) points were established on a calibration curve. These seventeen (17) points span a range of 5 nanograms to 5,000 nanograms of vinyl chloride in the chromatograph detector.

These chromatograph runs were made over a period of two days. It was noted that instrument drift from day to day was effecting experimental results. By running samples of the 789 PPM vinyl chloride calibration gas both days, a six percent (6%) deviation was seen in the response factor. 1CC of 789 PPM calibration gas was run both days. The average of four (4) runs on the first day gave a response factor of 5.7 counts per nanogram. On the second day 1 CC of the 789 PPM calibration gas gave an average of 5.4 counts per nanogram. This day to day instrument drift was noted several other times during the course of other portions of this study. To, compensate for this, a calibration run was made each day before running samples.

The data in Table #3 show there is an error in the preparation of some of the vinyl chloride and air mixtures. There is also a definite loss of sensitivity by the FID detector as the vinyl chloride concentration increases. Data from Table #3 are summarized in Table #4. When the response factor for all seventeen (17) points on the calibration curve are averaged, the response factor is 6.2 counts per nanogram, of vinyl chloride. (The maximum deviation from this mean of 6.2 is 40%).

How does this deviation effect the analytical results? By using data generated from an analysis of resin with low residual vinyl chloride, (sample wt., peak area, gas sample size) and using the two response factors at 6.2 as the mean and 8.7 as the maximum deviation, a residual vinyl chloride was calculated using the formula shown in Appendix 2.

Using the 6.2 response factor gave a residual vinyl chloride analysis of 6.09 ppm and using the 8.7 response factor results in an answer of 4.34 ppm. This is a 30% deviation in results. Consequently, if only one response factor is obtained for instrument calibration it would be possible to have a 30% error in data so obtained. This error could also be expected in the solvent method of analysis where an internal standard is used since the response to vinyl chloride is changing over the broad test range but it is not necessarily changing proportionally for the internal standard.

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Table 4

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Summary of Data in Table #3

<u>Nanograms Vinyl chloride On Detector</u>	<u>Chromatograph Peak Area</u>	<u>Response Factor (Area count/ Nanograms)</u>	<u>Average Response Factor</u>
4.8	42.1	8.7	7.9
6.3	48.3	7.6	
9.6	79.8	8.3	
12.7	89.5	7.0	
24	180	7.5	5.9
48	332	6.9	
127	637	5.0	
177	886	5.0	
254	1226	4.8	
400	2601	6.5	
507	2344	5.1	
1000	6048	6.1	4.8
1014	4644	4.6	
1400	8292	5.9	
2000	10884	5.5	
2535	10716	4.2	
5070	20184	4.0	

When it is realized that the response for vinyl chloride is not linear for this broad range of analysis, this problem can be dealt with. By dividing the response curve into smaller segments the deviation can be suppressed to a rather low value. For example, if Table #4 is divided into three (3) parts as shown and an average response factor calculated for each part, the deviation is reduced from 30% to 19%. This now gives a 9% deviation in the analytical results.

Using the same data as above and response factors of 7.9 for the average and 8.7 for the maximum deviation, the results now obtained are 4.78 PPM VCl and 4.34 PPM VCl.

At the high end of the response curve (in the area of 4000 PPM VCl) the response factor has more effect on the analytical results. In this range a deviation of 19% in response will give a 19% deviation in analytical results.

(11) Head Space Analysis of Geon 80X5 Resin:

The next step in our experimental plan was to expand the head space analysis into a typical production plant operation. Through John Whitney, the Avon Lake General Chemical Plant agreed to try the head space method of analysis. The analyses were run on samples of Geon 80X5 resin which were being dried in a small fluid bed still in J. Whitney's Lab. Samples were taken over time as the resin was being dried. In this way a large range of residual vinyl chloride was analysed. Samples were analysed for residual vinyl chloride in triplicate. The General Chemical Plant lab analysed samples both by the vapor space method and by the solvent method. Also, the Technical Center was given a similar set of samples for analysis by the vapor space method. All analyses were run in duplicate. The vapor space analysis in the General Chemical Plant lab was restricted to some extent. We could not use the conditions for analysis which we had used at the Technical Center, but had to use the conditions set up for the solvent method. That

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The data from this experiment are tabulated in Table #5 below.

Table 5

Sample Identification	<u>Head Space Method</u>		% Difference Between TC & ALGC	AL Gen. Chemical Solvent Method Results
	Technical Center Results	AL Gen. Chemical Results		
80X5 Run #3 1A	1584	2008	} 24%	2368
" " " 1B	1503	2055		2363
" " " 2A	1424	1650	} 16%	2015
" " " 2B	1423	1730		1995
" " " 3A	696	743	} 10%	869
" " " 3B	660	755		902
" " " 4A	342	390	} 12%	433
" " " 4B	343	391		433
" " " 5A	199	223	} 11%	198
" " " 5B	197	221		180

Samples are in duplicate. 1A & 1B are two samples at the same point on the drying curve.

These data shows rather good correlation between the Technical Center results and Avon Lake General Chemical Plant's results although the General Chemical results are consistently higher than the technical Center results. It was noted during the analysis that the system used in the General Chemical lab (solvent system) was not giving good separation of other volatile components in the resin. There were at least two side peaks on the vinyl chloride peak which were being integrated into the vinyl peak area. This could very well account for the high results from the General Chemical analysis. (It was later determined by J. Whitney that one of these side peaks was xylene used in charging catalyst to the 80X3 polymerization.)

The above experiment did not cover the low range of residual vinyl chloride due to a problem with the heat exchanger in the fluidizing silo. It was therefore agreed to make another run similar to this first one and attempt to get samples down in the low PPM residual vinyl chloride. Again Geon 80X3 was the resin used. Data from these runs are tabulated in Table #6 below.

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Table 6

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Sample Identification	Head Space Method		% Difference T.C./ALOC	AL Gen. Chem. Solvent Method Results
	Tech. Center Results	AL Gen. Chem. Results		
80X5 Run #4 1A	off scale	1889		3852
1B	1833	1874	3%	3118
2A	1538	1643	4%	2474
2B	1514	1547		2467
3A	922	975	3%	1597
3B	978	976		1594
4A	647	631	.5%	996
4B	599	608		974
5A	433	423	.2%	497
5B	398	410		420
6A	294	289	1%	298
6B	287	284		294
7A	not run	200		354
7B	not run	198		314
8A	136	126	10%	140
8B	144	129		135
9A	101	93.0	4%	91
9B	94.1	95.4		102
10A	22.8	18.1	19%	24
10B	21.1	17.6		26
11A	5.7	5.9	1%	Less than 1
11B	5.9	5.8		Less than 1

These data show very good agreement between the General Chemical lab results and the technical Center data. One reason for this better agreement was due to a change in the chromatograph conditions in the General Chemical Plant's lab. The carrier gas flow had changed enough to give better separation of the vinyl chloride from the other volatiles in the resin. This agreement could be improved more if the conditions were changed on the ALOC chromatograph and brought more in line with the conditions we have suggested.

(iii) Time Dependency of VCM equilibrium in Head Space

Two small scale experiments were conducted next. The first was to verify that equilibrium was established in the sample vial in fifteen minutes. Data from this experiment are shown in Table #7 below. These data clearly shows we have reached equilibrium with the vinyl chloride in the head space and resin in ten (10) minutes as A. Berens stated. The data also demonstrate that this equilibrium is held for at least twenty-five (25) minutes.

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Table 7

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<u>Sample Identification</u>	<u>Sample Wt.</u> <u>(gms)</u>	<u>Sample Size</u>	<u>Parts per Million</u> <u>Vinyl Chloride</u>
*10 min. in air oven	2.5855	.3 cc	78
14 min. in air oven	2.5892	.3 cc	76
15 min. in air oven	2.3550	.3 cc	83
17 min. in air oven	2.5833	.3 cc	79
20 min. in air oven	2.4633	.3 cc	77
25 min. in air oven	2.3732	.3 cc	84
Average			79
Maximum deviation			6%

*Resin used was a production sample of Geon 90X5
Response factor for this run was 5.27.

(iv) Comparison of Head Space and Solvent Method:

The second experiment of interest was an analysis of a resin sample and powder compound made from this resin. Geon 103EP F76 resin was compounded into a customer's formulation at the customer's plant. Samples of the resin and compound were analyzed for residual vinyl chloride. The data from these analyses are shown in Table #8. This particular resin sample gave two chromatograph peaks in the area of the chromatogram where vinyl chloride elutes. A mass spectre of these two peaks identified one peak as vinyl chloride and the other as methanol. The methanol present in this resin sample is in a large enough quantity to interfere with the vinyl chloride analysis. As to how much interference is being encountered is not known. (3)

A similar experiment has been run using 103EP F76 resin without methanol in it. This resin was compounded at the Technical Center into Geon 85707 powder compound. Samples of the resin were analyzed before compounding and also samples of compound that reached different temperatures in the compounding process were analyzed. These data are also shown in Table #8. The data show a significant amount of the residual vinyl chloride is lost in the compounding process. There are not enough data to make any judgment as to how consistent this loss would be in a production operation.

Data is also presented in Table #8 of analyses of these samples using the solvent method. The most striking thing about this data is the poor correlation of the headspace method with the solvent method data.

Several more experiments had been planned before concluding this work. One experiment was to find out the absoluteness of this method. The other as mentioned above was to look at the effect of other volatile materials in resin to see what effect they have on the vapor space analysis. These experiments could not be done as we have no instrument at this time to conduct these tests.

- (3) An experiment has been set up to investigate the effect of other volatile components in resin samples. This work is not being done as we do not have an instrument available at this time.

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Table 8

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Sample Identification	Head Space Method	Residual VCI	Residual VCI
	Residual VCI	Solvent Method	Solvent Method
	Tech. Center Results	ALOC Results	Tech. Center Results
103EP F76 Resin - A	3		22
103EP F76 Resin - A	3.2		
Compound from hopper	2.7		21
Compound from hopper	2.7		
Compound from Cooler	1.7		34 - 32
Compound from Cooler	1.6		38 - 18
103EP F76 Resin - B	30	91	98
	* 31		96
	34		
	30		
85707 Compound @ 1:0 ^o F	37	52	80
	33		64
	* 39		
	36		
85707 Compound @ 250 ^o F	1.9	3	22
	1.9		5
	* 2.7		
	2.6		

* Represents duplicate runs on duplicate samples

Experimental Results

Direct Method of Analysis

(1) Reproducibility of Analysis

The data presented here were generated using the procedure described in the Appendix of this report. As indicated in the analytical procedure, the difficulty with this test is the operation of the chromatograph. The cooling of the chromatograph column would be a problem if this test were used in production plants.

This test also requires a more accurate weight measurement of the sample to be analyzed. An error of one (1) milligram in weighting would give a 10% error in the analytical results.

The initial evaluation of this test method was a determination of the reproducibility of the method. A sample of Geon 110K233 resin was chromatographed nine (9) times in two days. This resin was reported to have 90 PPM residual vinyl chloride by the Avon Lake General Chemical Plant using the solvent method of analysis. Since no calibration curve had been established for this test as yet, all calculations are based on the General Chemical Lab results of 90 PPM residual vinyl chloride. Data from this experiment are tabulated in Table #9 below.

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Table 9Reproducibility of Direct Method of Analysis of Geon 110X222

<u>OC Run No.</u>	<u>Sample Weight</u>	<u>OC Peak Area</u>	<u>Apparent PPM VCl *</u>
1	.02344	3603	87.98
2	.02224	3440	90.03
3	.02293	3766	92.55
4	.01080	2572	87.68
5	.01898	4733	91.78
6	.02594		
7	.02133	4762	88.00
8	.01918	4434	91.11
9	.01373	3169	90.97
Standard Deviation			1.9%

* This is only a relative measurement based on a reported VCM concentration in the resin.

The results shown in this table were arrived at by finding the average area per milligram of sample and dividing this number by 90 (90 PPM VCl reported monomer level in the sample) to obtain the area counts per milligram of vinyl chloride. This number was then used to determine the residual vinyl chloride in each sample run. This experiment was repeated using a different resin. A sample of Geon 222 resin was run five (5) times. The data from this experiment are shown in Table #10 below. This resin was reported to have 30PPM residual vinyl chloride by Avon Lake General Chemical.

Table 10Reproducibility of Direct Method of Analysis
Using Geon 222 Resin

<u>OC Run No.</u>	<u>Sample Identification</u>	<u>Sample Weight (gms)</u>	<u>OC Peak Area</u>	<u>Apparent PPM VCl</u>
1	Geon 222 resin	.02457	1632	29.81
2	" " "	.01955	1397	32.07
3	" " "	.02562	1609	28.19
4	" " "	.01986	1368	30.92
5	" " "	.01949	1261	29.05

Standard deviation 3.1%

* See footnotes, Table 9.

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Again these data shows the test method to give excellent reproducibility.

(11) Response Factors for VCH

In the next experiment we established a calibration curve for this method of analysis. The procedure for this was similar to the one used for the vapor space analysis. Vinyl chloride and air mixtures were prepared and injected into the chromatograph at different volumes. Prior to injecting any sample the column oven was cooled to approximately 40°C and the first two to three inches of the column frozen with dry ice. A time delay of one and one-half (1½) minutes was used to freeze the column. The sample of calibration gas was then injected and the chromatograph oven was heated very rapidly to 50°C to 200°C at 16° per minute. The vinyl chloride eluted from the column in six and one-half (6½) minutes.

The data from this calibration are tabulated in Table #11 below. These data are very similar to that generated for the vapor space method. There is an increase in detector sensitivity as the vinyl chloride concentration on the detector decreases.

Table 11

Calibration Curve for the Direct Method of Analysis

Chromatograph Run No.	Sample Gas	Sample Size (cc)	Vinyl Chloride in Sample (Nanograms)	Chromatograph Peak Area	Average Peak Area	Response Factor Counts/Nanogram VCl
3-29-74-9	Std @ 19 PPM VCl	.5	24.08	76		
3-29-74-10	Std @ 19 PPM VCl	.5	24.08	76	76	3.16
3-27-74-1	Std @ 19 PPM VCl	1	48.17	142		
3-27-74-2	Std @ 19 PPM VCl	1	48.17	142		
3-27-74-3	Std @ 19 PPM VCl	1	48.17	142		
3-27-74-4	Std @ 19 PPM VCl	1	48.17	142		
3-27-74-5	Std @ 19 PPM VCl	1	48.17	142	142	3.00
3-27-74-6	Std @ 79 PPM VCl	.5	100.15	245		
3-27-74-7	Std @ 79 PPM VCl	.5	100.15	241		
3-27-74-8	Std @ 79 PPM VCl	.5	100.15	243		
3-27-74-9	Std @ 79 PPM VCl	.5	100.15	245	244	2.44
3-27-74-10	Std @ 79 PPM VCl	1	200.3	520		
3-27-74-11	Std @ 79 PPM VCl	1	200.3	522		
3-27-74-12	Std @ 79 PPM VCl	1	200.3	518		
3-27-74-13	Std @ 79 PPM VCl	1	200.3	520		
3-27-74-14	Std @ 79 PPM VCl	1	200.3	518	520	2.99
3-27-74-15	Std @ 686 PPM VCl	.5	869.5	2074		
3-27-74-16	Std @ 686 PPM VCl	.5	869.5	2099		
3-27-74-17	Std @ 686 PPM VCl	.5	869.5	2074		
3-27-74-18	Std @ 686 PPM VCl	.5	869.5	2074	2070	2.98
3-27-74-19	Std @ 686 PPM VCl	1	1739	4104		
3-27-74-20	Std @ 686 PPM VCl	1	1739	4078		
3-27-74-21	Std @ 686 PPM VCl	1	No data septum locked			
3-27-74-22	Std @ 686 PPM VCl	1	1739	4104	4095	2.95
3-27-74-23	Std @ 789 PPM VCl	1	2001	4842		
3-27-74-24	Std @ 789 PPM VCl	1	2001	4842	4842	2.42

Average of all response factors

2.62

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(111) Comparison of Head Space Method and Direct Method of Analysis:

The next experiment run was comparison of the two methods of analysis. Several samples of Geon resin were run using both methods of analysis. The data from this experiment are tabulated in Table #12 below.

Table 12

A Comparison of Results of the Two Methods of Analysis

<u>Sample Identification</u>		<u>Results From Vapor Space Analysis (PPM VC1)</u>	<u>Results From Direct Method of Analysis (PPM VC1)</u>
103EP 776 Bin #1	1515 hrs.	30	30
		31	29
		31	20
		29	24
		30	
		29	
103EP 776 Bin #1	1350 hrs.	27	
		46	47
		45	45
Geon 110X253		43	48
		58	2
		50	

Considering that the data shown in Table #12 were generated using two very different methods of analysis, the data shows very good correlation between the two test methods. This correlation is indicating that both methods are rather close to an absolute value. However, the data are not sufficient to say that the average values for the three resin samples in Table #12 are in fact the absolute residual vinyl chloride.

From the data generated to date it appears that more information is needed to establish any test method with the degree of accuracy required by the situation as we know it today (the continuing tightening of government restriction). I am referring to all of the unknown which have come to light during this investigation, such as polymerization components eluting along with the vinyl chloride.

The author acknowledges the experimental work of Ray Whitaker who performed most of the gas chromatograph analyses referred to in this report and Mike O'Hara for his help in editing and administration of the report.

Appendix (1)

Response Factor Calculations

Response Factors for 19 ppm VC1 19cc of VC1 in 1,000,000 cc of sample

or:

$$\frac{19\text{cc}}{10^6\text{cc}} = \frac{x}{1\text{cc}} \quad \text{where } x \text{ equals the cc's of VC1 in 1 cc of calibration gas}$$

solving: $x = 19 \times 10^{-6}$ cc of VC1 in 1 cc of 19 ppm calibration gas

$$\text{by gas law: } \frac{6.2 \times 10^4 \text{ milligrams VC1}}{(1) 2.443 \times 10^4 \text{ cc}} = \frac{x \text{ milligrams VC1}}{19 \times 10^{-6} \text{ cc}}$$

solving: $x = 48.17 \times 10^{-6}$ milligrams or 48.17 nanograms in 1cc of 19 ppm VC1 calibration gas

(1) Standard volume corrected to room temperature

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Appendix (2)

Analytical Procedures

1. The head space Analysis

The gas chromatograph (GC) to be used for the analysis is set up with the following conditions:

- a) 1/8 inch x 8 ft. stainless steel column packed with 80/100 mesh Porapak Q8.
- b) The gas flows are adjusted to obtain the recommended settings prescribed by the GC manufacturer (Hewlett-Packard) helium 30 cc/min - hydrogen 30 cc/min - air 240 cc/min.
- c) GC temperature settings are:

injection port	150°C
detector	250°C
oven	160°C

After the above conditions have been set and the chromatograph has stabilized at these conditions the instrument is ready for calibration (determination of instrument response factor).

Prior to analysing any resin sample, a response factor must be calculated for the gas chromatograph which is to be used. This is done by using two gas mixtures of vinyl chloride and air of known concentration. One sample at a low concentration (about 20 ppm VCl) and one sample at a high concentration (about 1000 ppm VCl).

The calibration gas mixtures are bought as compressed gas in a cylinder. To use them a glass sample vessel of about 1 liter is needed. For our work we used a 1 liter cylindrical separator funnel with a stop cock at both ends. A glass septum stem was also fitted to one end of the vessel for removing syringe samples from the vessel.

The sample vessel is fitted with a septum and both stop cocks are opened. The low concentration vinyl chloride gas is purged through the vessel at about 5 liters per minute for about one minute. Then both stop cocks are closed sealing the vessel with the gas sample in it. The stop cocks are closed in such a manner as to eliminate a pressure buildup in the vessel. That is, the stop cock nearest the gas cylinder is closed first and then the exit stop cock is closed.

The needle of a 1cc gas syringe is inserted through the septum into the sample vessel and the syringe plunger drawn back as far as it will go. The syringe is left in this position for five seconds to allow the sample gas to fill the syringe. After the five second delay, the needle is withdrawn from the septum and the syringe plunger is moved to read exactly 1 cc. This gas sample is then injected into the chromatograph injection port and the GC recorder started.

" peak area counts per milligram vinyl chloride (response factor)

milligrams of vinyl chloride in sample injected (X above)

" the milligrams of vinyl chloride in the sample injected to them divided into the average peak area count to give counts of peak area per milligram of vinyl chloride

" Standard volume corrected to room temperature

" (the vinyl chloride in sample injected) as vinyl chloride in syringe (X above)

(2) Determination of the weight of vinyl chloride in the gas chromatograph samples run: (by the gas law)

X = cc vinyl chloride in the syringe sample

also
syringe sample

vinyl chloride concentration in the sample (X above)

(1) Determination of the volume of vinyl chloride in the gas chromatograph samples run:

From this data the following calculations are made to determine a response factor for vinyl chloride.

The four chromatograph peak areas found for each of the three different samples run are averaged together to give an average peak area for each of the three samples run.

When these runs are completed, following the same procedure as previously used, draw out in excess of .5 cc from the sample vessel filled with the high concentration of vinyl chloride. After removing the syringe needle from the sample vessel bring the plunger to read exactly .5 cc and inject this sample into the chromatograph. Do this at least four times.

Again draw out in excess of 1 cc from the sample vessel with the same gas syringe as used above and following the same procedure as used for the low concentration vinyl chloride make four chromatograph runs with this sample gas mixture.

After these runs are completed, recharge the sample vessel using the same procedure as given above only use the high concentration vinyl chloride gas mixture. Do this at least four times.

In approximately three minutes (depending on the specific GC column) the vinyl chloride peak will elute. After the vinyl chloride peak elutes wait one minute and repeat the above sampling procedure of charging 1 cc of the low concentration vinyl chloride to the chromatograph. Do this at least four times.

From the three different samples of vinyl chloride gas mixtures run, three response factors are determined. These three factors are averaged together to obtain a response factor for calculating residual vinyl chloride in a sample.

To analyze a resin sample for residual vinyl chloride, weigh approximately 2 grams of the resin into a vial of known volume (We have used a 12 cc vial fitted with a removable septum cap. This gives a weight to volume ratio of 1 to 6 which worked well in our analysis.) Seal the vial with a septum and place in an air oven controlled at 90°C. Leave the vial in the oven for fifteen minutes. After the fifteen minute heating time, remove the vial from the oven and draw out a sample of the gas from the top of the vial with a gas syringe. Inject this sample into the chromatograph. The sample size injected depends on the amount of residual vinyl chloride in the resin. In the range of 1000 ppm to 100 ppm .3 cc is sufficient. In the range of 100 ppm to 1 ppm .5 cc is sufficient. The vinyl chloride peak will elute in approximately 3 minutes.

One minute after the vinyl chloride peak elutes from the GC column another sample can be injected.

To calculate the residual vinyl chloride in the resin sample the following data are needed:

1. Response factor for vinyl chloride
2. Weight of the polyvinyl chloride resin in vial (gms)
3. Size of the sample injected into the chromatograph (cc)
4. Area of the chromatograph peak for the vinyl chloride from the sample.
5. Volume of the sample vial (cc)
6. Atmospheric pressure (barometric pressure).

These data are combined in the following equation to give the residual vinyl chloride for the sample in parts per million.

Residual Vinyl Chloride New Program

$$\begin{array}{c}
 \text{Residual Vinyl Chloride (ppm)} = \frac{\text{Area} \times \text{Volume} \times \text{Response Factor}}{\text{Weight} \times \text{Injection Volume}} \\
 \text{Area} = 1.5 \times 10^4 \quad \text{Volume} = 0.3 \text{ cc} \quad \text{Response Factor} = 1.15 \times 10^4 \\
 \text{Weight} = 2 \text{ gms} \quad \text{Injection Volume} = 0.3 \text{ cc}
 \end{array}$$

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Analytical Procedure for Direct Method of Analysis2. The Direct Method of Analysis

This method also requires a response factor to be calculated prior to analyzing any samples for residual vinyl chloride. This is done in the same manner as used in the vapor space analysis above. The only difference being the way the chromatograph is run.

The chromatograph is set up with the same column and conditions as used in the head space analysis except that the column are then cooled with dry ice for one and one half (1½) minutes. The standard gas sample is then injected on to the column and the oven temperature is brought rapidly to 50°C. At 50°C a temperature program is started on the column oven to raise the temperature to 200°C at a rate of 16° per minute.

Using this method the vinyl chloride elutes from the column is approximately 7 minutes. With these conditions the three standard vinyl chloride air samples are run to produce a response factor. After this calibration is completed the instrument is ready to run samples.

To analyze for residual vinyl chloride in resin with this method, a small sample of the resin (.01 to .03 gram) is weighed into a 4 mm glass tube 95 mm long. The sample is positioned in the tube 50 mm from the bottom by a glass wool plug. With the chromatograph column oven at room temperature and the first two to three inches of the column cooled with dry ice, the septum is removed from the injection port and the sample tube dropped in. The port is then resealed with a septum and the analysis started. The oven program is initiated when the oven temperature reaches 50°C. In approximately 7 minutes the vinyl chloride peak will elute from the column. As soon as the vinyl chloride peak has eluted, the sample tube is removed from the injection port and the port resealed.

Evaluation of this method has been conducted using a Hewlett-Packard 5710 gas chromatograph equipped with a flame ionization detector (FID). This chromatograph is ideally suited for this analysis as the injection port is in a vertical position allowing the glass sample tube to be dropped into the port and positioned by gravity. The glass wool holds the sample in the center of the heated area of the injection port. It is the heat of the injection port (150°C) which drives off the residual monomer. The chromatograph carrier gas then sweeps the monomer onto the column for separation and detection. The FID detector allows the flow of carrier gas (helium) to be interrupted when the sample tube is inserted into the injection port without harming the detector.

To calculate the parts per million (ppm) vinyl chloride in the resin samples using the method, the following calculations are made:

- (1)
$$\frac{\text{Peak area of vinyl chloride}}{\text{Response factor}} = \text{nanograms vinyl chloride in sample}$$
- (2)
$$\frac{\text{Nanograms vinyl chloride in sample}}{\text{weight of sample (in milligrams)}} = \text{ppm vinyl chloride in sample}$$