AIRCO, INC.

A. M. Taylor
Murray Hill

I. J. Nelsen & F. Golleb
Murray Hill

June 20, 1962

ANALYSIS: VINYL CHLORIDE MONOMER

On June 8, 1962, I. J. Nelsen and F. Golleb visited L. Mikkelsen, Manager of Applications, of the F&M Scientific Co. at Avondale, Pa. Mr. Mikkelsen had been previously employed by the Kennabis Company, and had presented a technical paper* on the use of gas chromatography for the determination of trace impurities in vinyl chloride. Mr. Mikkelsen's paper is the only reference disclosed in a search of the literature, and since he is now employed at F&M where we have friendly contact, the visit was conveniently arranged.

Discussion

Mr. Mikkelsen first showed a chromatographic trace in which the following impurities in vinyl chloride were detected:

	Retention Time, Min.	Concentration PPM
Methyl chloride	6	Not measured
Vinyl chloride	8	Major constituent
Vinyl acetylene	14 1/2	3.8
Ethyl chloride	16 1/2	5.8
Vinyl bromide	21 1/2	0.4
Vinylidene chloride	31	0.3
Hexane 1**	37	2.5

** Hexane 1 was used as an internal standard and was not present in the vinyl chloride.

These have been determined in a typical sample of liquid vinyl chloride made by the Ethyl Corporation. Since the original purpose of the examination had been to detect acetaldehyde, and none was detected, no attempt was made to measure additional impurities which are lower boiling than vinyl chloride. (Methyl chloride was detected but no quantitative answer was obtained because it was lower boiling). It is interesting to note that the identities of the individual impurities after separation were determined by mass spectrometry and confirmed by retention time.

* Presented at Pittsburgh Conference on Analytical Chem. and Applied Spectroscopy, Feb. 29 - Mar. 4, 1960

Card 11 3/7/60 Lowry Preston Abstracts Code 88-36-61

Liquid samples were introduced into the chromatograph by chilling a syringe in Dry Ice, pouring vinyl chloride from a beaker into the syringe, replacing the plunger and then injecting into the chromatograph. Mikkelsen believed that evaporation losses were negligible.

The apparatus with which these analyses were conducted was a "double chromatograph" constructed by Mr. Mikkelsen. This embodies essentially the same principle and design as the double chromatograph described in Aireo Report C2D-62-042 dealing with the determination of carbonyl sulfide in carbon dioxide. Both columns were 10 feet long, packed with dibutyl maleate on chromasorb and were operated at 30°C. The first or preparative column was 1/2" O.D. while the analytical column was 1/4" O.D.

Action Taken

Dibutyl maleate column packing and small samples of the listed impurities have now been ordered. When they are received, we will attempt to duplicate the retention time and separations. However, our recent successes with the use of the flame ionization detectors make us hopeful that we can achieve a sensitivity equal to that of Mikkelsen without the use of a preparative stage in the chromatograph.

I. J. Nelsen

F. Golleb

IJN:agr
FG

cc: A. Muller
E. R. Blanchard
P. W. Townsend
R. L. Siegman

DIVISION

CUMBERLAND

DELIVER THIS LETTER TO	ADDRESS REPLY TO
Mr A. H. Taylor	Mr. C. A. Cook
At Murray Hill	At Calvert City

Date June 18, 1962

Replying to your letter dated

SUBJECT: GAS CHROMATOGRAPHIC ANALYSIS OF VCl

At the present time at Calvert City we are analyzing the inlet and exit of our vinyl chloride monomer reactors via gas chromatography. For this analysis we use a Perkin-Elmer 154-C gas chromatograph containing a 6 foot ¼ inch stainless steel column packed with Florapak 80 coated with 20% Silicone DC 200. With a temperature of 35°C., inlet pressure of 5 psi, and 8.2 volts bridge current, air has a retention time of 0.85 minutes, C_2H_2 1.30, HCl 2.50, and VCl 5.4. Chlorine may also be separated on this column, having a retention time of 4 minutes.

While coating 20% liquid substrate on teflon supposedly impossible, we have found that this weight per cent gives us better results than the recommended 10% level. We have also used Silicone DC 220 and found it to be suitable. While we have not tried it, several people have claimed that freezing the teflon prior to preparing columns makes it easier to handle. We have not tried any columns longer or shorter than the present 6 foot column, but have investigated temperature and flow rate and find that the present values give us the best results.

Greenbrier Instruments Company in one of their process gas chromatographs separates N_2, VCl, HCl, and C_2H_2. Using a 12 foot silicone on teflon column at 57°C., current of 18 ma., and 60 cc/min. carrier flow, N_2 has a retention time of 1 minute, C_2H_2 1.8, HCl 2.0, and VCl 4.0.

At the recent ISA symposium in Charleston, W. Va., I was talking to some people from Monsanto's Texas City plant and they claimed that DuPont T-6 grade teflon was the best to use for VCl work. They also mentioned that sometime in the near future their group will be publishing a paper on the analysis of VCl by gas chromatography.

For work in gas analysis from the stripping section of our polymer plant we use a Perkin-Elmer K_X column (Carbowax 1500) to analyze gas samples containing 90% VCl. At 70°C., 10 psi inlet pressure, and 8.2 volts, VCl has a retention time of 1.3 minutes, acetaldehyde 4.0, acetone 6.0, vinyl acetate 9.0, and trichloroethylene 13.0.

June 13, 1962

B. F. Goodrich has recommended the use of a 20 foot ¼ inch column containing 30% Armeen SD on chromosorb. At a temperature of 88°C., they claim the following retention times: propene 2.4 minutes, methyl chloride 3.25, VCl 3.40, ethyl chloride 6.40, 2-chloropropene 7.7, 7 Br 8.8, VCl_2 12.2, 3-chloropropene 14.2, 1,1 dichloroethane 20.2, and chloroprene 22.0.

We have obtained a column of the above type for evaluation on our Micro-Tek instrument but have not found time to do so yet. We also have a 20 foot ¼ inch column containing 10% Armeen SD on teflon which we want to try out.

C A Cook

C. A. COOK

CAC:mja

cc: R. L. Siegmann

ARCAC

A. H. Taylor — Murray Hill

R. L. Siegmann — Calvert City

June 25, 1962

ANALYSIS: VINYL CHLORIDE MONOMER

I read with interest the trip report by I. J. Nelson and F. Golleb. About a year ago, I discussed Mikkelsen's paper with Bill Morris, Chief Chemist at Goodrich. He stated that Goodrich investigated the procedure and did not like it. Consequently, their research group proceeded in other directions, resulting in the chromatographic method using Armeen SD on chromosorb, described in C. Cook's letter to you, 6/18/62.

This method is now in use by Goodrich at Calvert City. They are performing this analysis on a Beckman GC-2A using thermal conductivity detection. Recently, they have equipped this unit with a hydrogen flame detector and a temperature programmer. I know they planned to evaluate their method using the hydrogen flame detector, but have not heard their results.

From the scans I have seen, they have a problem with VCl tailing, but are reporting results as low as 2 ppm. As did Mikkelsen, they identified impurities by mass spectrometry. My information is that their Louisville lab has detected some 40 impurities and identified about 20. We plan to try Armeen SD on Teflon, with the hope of reducing the tailing of VCl. Goodrich has not tried this yet.

Goodrich uses Micro-Tek snap samplers which are excellent for vinyl chlorides. Ethyl Corporation also uses Micro-Tek hardware - snap samplers and the Micro-Tek liquid sample valve. I understand Micro-Tek worked closely with Ethyl and is working with Monsanto at Geismar, La. We have had no success in extracting information from Micro-Tek, for they claim they have had no clearance to release such information, but are trying to get a release from Ethyl.

Attached for your information is a recent analysis of Ethyl Corporation's vinyl chloride and monomer from Goodrich. Both monomers were made via the ethylene dichloride route.

RLS:mja
Attachment
cc: I. J. Nelson
F. Golleb
A. Miller
E. E. Blanchard
P. W. Townsend

R. L. SIEGMANN

VINYL CHLORIDE

	Ethyl	Goodrich
Acidity, as HCl, ppm	0.0	0.0
Acetylene, ppm	0.0	0.5
Acetaldehyde, ppm	0.0	0.8
Iron, ppm	0.1	0.01
Water, ppm	14.0	174.0
Non-volatiles, ppm	6.0	10.0
Peroxides, as H_2O_2, ppm	0.01	1
Sulfur, ppm	0.0	0.07
Dorell Weathering, %.	0.1	0.3
Polymer Conversion, %	95.1	95.0
Resin Viscosity	2.86	2.83
Vinyl Acetylene, ppm	0.05	-
1,1-dichloroethylene, ppm	0.00	-
1,1-dichloroethane, ppm	0.00	1
1,2-dichloroethane, ppm	0.00	-
Ethyl chloride, ppm	0.34	25.0
3-chloropropene, ppm	-	3.0
Dichloromethane	-	3.0
Chloroprene	-	9.0
Propane	-	1
Methyl Chloride	-	61.0
Vinyl Bromide	-	26.0

FILE

ARCAC

G. T. Cole — New York

R. L. Siegmann — Calvert City

2/14/62

J. P. FRANK - VINYL CHLORIDE CLAIM — 2/12/62

We have stated many times before that the sampling and analysis of vinyl chloride monomer is not as simple as it looks. Even with carefully controlled and standardized procedures, it is almost impossible to duplicate results within normal analytical limits. Our friends at Goodrich also agree with this premise. However, analysis for water in vinyl chloride - under almost any reasonably diverse conditions - will not lead to a difference of 0.3% in the results of two tests.

The standard method in the industry for water in vinyl chloride is the Karl Fischer method. Variations in techniques employed to avoid atmospheric moisture contamination are widespread, but even here, the spread from the best method to the worst method is only in the order of 0.02%.

The sampling technique is an additional source of error - but if one uses a bomb - which is standard - and takes reasonable precautions to avoid contamination, results obtained by the different sampling techniques should not differ by more than a few hundredths of a per cent.

Sampling in open containers - such as a Dewar flask - does lead to very high results in the analysis for water, and, of course, failure to purge sample lines will do the same.

Attached is our current procedure for sampling and analysis for water. Pertinent comments have been added to indicate critical points.

I might add that the tank cars in question were sampled after filling was completed and the sample obtained via the sampling device on the car. This device removes a sample from a well in the car bottom.

R L

R. L. SIEGMANN

RLS:mja
Attachments
cc: B. H. Krashin - NY
P. E. Evers - NY
M. L. Jaffee - NY
B. V. Coles - NY
R. F. Causaway - CC

CUMBERLAND CHEMICAL CORPORATION

AM 6000 - C 4

FILE

Vinyl Chloride: Analysis for Water

Sampling Procedure

1. Purge sample line by venting monomer until liquid monomer begins to discharge. (If sampling tank car, use sample connection, not gauging device.)

2. Immediately connect a clean, dry pressure cylinder which has previously been evacuated. Open the inlet valve and obtain sample.

3. Close valve and disconnect cylinder from system.

Notes: 1. If a larger sample is desired, the evacuated cylinder can be cooled by holding it in the stream of vinyl chloride during purging of sample lines, but be sure cylinder is properly grounded.

2. Where gravity flow is possible, the cylinder should have one valve connected to a dip leg, and the cylinder filled on a weight basis.

3. Excessive flushing through the cylinder results in concentrating higher boiling impurities such as acetaldehyde and water within the cylinder. The procedures above eliminate this hazard.

Analytical Procedure

Reagents:

1. Dry Methanol
2. Karl Fischer Reagent (Single solution, stabilized)

Apparatus:

1. Fisher "Dead Stop" titrimeter (Wilkens Anderson Co.)
2. Titration vessel
3. Mettler Gramatic "600" balance

:M 6000 - C 4 (Cont'd)

'nalytical Procedure (Cont'd)

Procedure:

1. 'ry electrodes and stirrer with Kleenex. Dry titration vessel in oven at 105°C. and cool in 'esiccator.

2. 'dd 50 ml of methanol to dry titration vessel nd run a blank. (Upper dial at 70, lower dial at 35.) un to a 20 second endpoint.

3. Add 50 ml of methanol to a second dry titration vessel, tare on balance and add 30 grams of vinyl chloride after insuring that the sample cylinder nipple is clean and dry.

4. Immediately connect vessel to ace titrator and stopper. Titrate using same settings as in the blank determination and to a 20 second endpoint.

Calculations:

$$H_2O,\ ppm = \frac{(ml\ KF\ for\ sample - ml\ KF\ for\ blank) \times (H_2O\ factor)}{eight\ of\ Sample} \times 10,000$$

H_2O factor: Determine by proceeding as for blank determination. hen endpoint is reached, weigh in one drop of water from a weighing bottle or from a vial fitted with a medicine dropper mounted in a cork stopper. Titrate to end point as above. Use this titration for calculating factor.

$$H_2O\ factor = \frac{grams\ of\ H_2O}{ml\ KF} \times 100$$

Notes: 1. hile many laboratories neutralise the water in the methanol solvent before adding vinyl chloride - instead of running a blank - it has been found that high results are obtained, particularly on high humidity days. At the end point, a slight excess of KF reagent is present which rapidly reacts with atmospheric moisture during the subsequent handling.

AM 6000 - C 4 (Cont'd)

Analytical Procedure (Cont'd)

Notes: (Cont'd)

2. If a Mettler "600" balance is not available for rapid weighing, cylinder can be weighed before and after adding the monomer to the titration vessel. eigh to ± 0.1 gram.

3. The vinyl chloride will boil off from the vessel during the procedure, effectively blanketing the system and avoiding atmospheric contamination. The water from the vinyl chloride remains in the methanol. The vessel containing the methanol is not pre-cooled to prevent loss of monomer because the RF reaction rate is extremely slow at low temperatures.

4. Titration to a visual end point can be used with resultant loss in accuracy.

APPROVED _____

CUMBERLAND

R. L. Siegmann (2)
Calvert City

C. A. Cook
Calvert City

February 23, 1961

Cost of VCl Monomer Analysis

In determining the cost of a laboratory analysis of vinyl chloride monomer shipment samples, the following times for analysis were used:

Aldehydes	45 minutes
Acid and C_2H_2	60 minutes
Turbidity	10 minutes
Conversion	95 minutes
Non-volatiles	35 minutes
Water	35 minutes
Dorell Weathering	20 minutes
Iron	45 minutes
Resin Viscosity	35 minutes
Bomb Cleanup	5 minutes
	385 minutes Total

In addition, 15 minutes is allowed for laboratory observation of sample pulling, giving a total time of 400 minutes. This is actual working time and does not take into account the many waiting periods that occur during a monomer analysis such as allowing the VCl to vaporize off, polymerization time or freeze-thaw time in polymer conversion test. Time has been allowed for the preparation of reagents and apparatus cleanup in all cases where required.

At a cost of analysis of $4.59 per hour (the figure supplied by Accounting Department) a total analysis time of 400 minutes would put the cost of a VCl shipment analysis at $32.63.

It is felt that in general all time figures are on the conservative side and would only be attainable by a technician under optimum conditions.

This figure of $32.63 per shipment analysis would apply to one sample being carried all the way through. Obviously if several samples were run at the same time, some savings would be noted. Also this data assumes that the monomer is uninhibited. If the monomer was inhibited the cost of analysis would be significantly higher.

CHARLES A. COOK
Project Chemist

CAC:mja

CUMBERLAND

F. Wood
Calvert City

C. A. Cook
Calvert City

May 10, 1962

VINYL CHLORIDE CATALYST

The following is for your information:

A. Catalysts for VCl. I Calculation of the Complicated Reaction Equilibrium in the Synthesis of VCl. The specific action of sublimate catalyst. Janda, Chemi. zvesti 11 15-23 (1957)

Kp values experimentally found in the synthesis of VCl from C_2H_2 and HCl with HgCl2 and active C as catalyst, were compared with the theoretical thermodynamic values. The equilibrium composition in the reaction mixture at 350-550°. K was calculated. Even at the initial mole ratio VCl = 1:1, the conversion of C_2H_2 to VCl decreases permanently with the increasing temperature, and the conversion to 1,1-dichloroethane (II) first slightly increases and at temperatures about 230° decreases rapidly. This was found to be true by experiment. By comparing the theoretical calculations with practical results in the formation of II in the excess of HCl the selective effect of the catalyst ($HgCl_2$ on active C) was determined in the reaction forming VCl.

B. II Increasing the Activity of the $HgCl_2$ Catalyst by the Addition of Inorganic Acids. Effect of the carrier of the catalyst salt on the activity and selectivity of the catalyst. Janda & Vanko, Ibid 248-58

In the synthesis of VCl from C_2H_2 and HCl, the activity of the $HgCl_2$ catalyst is increased by the addition of equimolar amounts of H_3PO_4, and $HClO_4$ to the $HgCl_2$ on active C. The increase in activity of the catalyst is dependent upon polarity of the acid and increases in the order $H_3PO_4 < H_2SO_4 < HClO_4$. The chemical nature of the mercuric salt does not affect the selectivity of the catalyst. The type of active C used to prepare the catalyst does affect the activity as well as selectivity. The higher the amounts of iron and zinc in the active C, the higher the formation of higher boiling by products.

C. III Conditions for Development of Side Reaction Products. Ibid 660

VCl, synthesised above 150° on a catalyst prepared by impregnating active C with $HgCl_2$, contains from the products boiling above 20°, $MeCHCl_2$ (II) trans $(ClCH=)_2$ (III), AcH (IV) and in smaller amounts cis $(ClCH=)_2$ (IV), $ClCH_2CHCl_2$ (VI) and $CH_2=CCl_2$ (VII). In the system for the formation of IV and VII water is necessary. Formation of III, V, and VII is dependent on the amount of free chlorine in the HCl entering the reaction. In reaction of HCl with VCl, the formation of II, III, and VI and part of IV and VCl is catalyzed by the active C, while the other part of VCl and IV, VII, and V is catalyzed by $HgCl_2$.

D. IV Reaction Intermediates Formed During Synthesis in the Presence of Water. Ibid 12 37-47 (1958)

The preparation and properties of some unknown compounds formed during the synthesis of VCl on $HgCl_2$ catalyst in the presence of water are described. The formula for the final compound was found to be $OHCC(Hg\text{-}Cl)_2\ HgO\ HgC(HgCl)_2 - CHCl_2$. $HgCl_2$ catalyzes the formation of VCl even if not spread on matter having a large specific surface.

E. V Form of Inactivation of Hg Contact. Ibid 155-62

In the sythesis of VCl, the $HgCl_2$ catalyst is mostly deactivated by the excess and unreacted C_2H_2 and by the humidity of the reaction system. The decrease of catalyst activity caused by the pressure of $HgCl_2$ vapor is negligible in the praxis. The only significant reaction leading partly to the reduction of $HgCl_2$ to Hg_2Cl_2 and metallic Hg and partly to the formation of elementary C is the reaction between C_2H_2, $HgCl_2$, and water. This does not agree with finding of others.

G. A. COOK

CAC:mja

ARCO

L. Barnes, Jr. — J. Parker

Murray Hill — Calvert City

June 14, 1961

DETERMINATION OF ACETALDEHYDE IN VINYL CHLORIDE MONOMER

Thanks for the letter of May 31, Lou. A letter from you is always welcome --- even one that requires an answer.

But before answering your questions, I would like to inject some comments. First of all, I have no quarrel with the 2-methylindole method --- it has been in use for a long time and enjoys a good reputation. Why then develope a "gadget" method that smacks of hieroxancy? Simply because it has the following advantages over the turbidimetric procedure.

1. The polarographic method is five times faster.
2. The reagents are stable.
3. It is a simpler procedure with fewer steps.
4. It appears to be more reproducible.
5. It can quantitatively separate mixed aldehydes. (see attached chart)
6. It can determine from 0.5 to over 1000 ppm aldehyde without the necessity of diluting or otherwise juggling the sample size.

But lets get down to cases. The 2-methylindole procedure requires about 3 hours for completion as compared with 30 minutes for the polarograph. And if the aldehyde content goes much above 10 ppm the 2-methylindole procedure has to be repeated --- another 3 hours lost.

As an example. Recently the lab received a monomer sample containing gross amounts of aldehyde. The shifts made two attempts to obtain results using the turbidimetric method --- only to end up titrating the sample. Therefore it took some 6 hours to find an approximate answer as far as the acetaldehyde of the sample the polarograph g[illegible]

While it is true that in any method speed should be ancillary to accuracy, wouldn't it be nice to have an aldehyde method that is both fast and accurate?

But before I get completely carried away let's get on with answering your questions.

Answer to question No. 1

From the data we have gathered so far the polarographic method appears to be reproducible within 0.3 ppm as compared with 1.0 ppm for the turbidimetric method.

Answer to question No. 2

The polarographic results are not always higher. See the attached results.

Answer to question No. 3

Calibration curves for both methods were prepared using acetaldehyde-ammonia complex. These curves are attached.

As a check, some acetaldehyde (Eastman) was added to vinyl chloride monomer and determined using both methods. The results on repetitive samples run independently were:

polarograph	2-methylindole
8.2 ppm	6.3 ppm
8.5	7.2
8.5	

Answer to question No. 4

A mistake was made in the 2-methylindole procedure sent to you. We no longer add the 10 ml of water to the 1 ml of concentrated ammonium hydroxide.

And now for some results.

When we first developed the method we took a sample of monomer and ran several independent analyses. The results were:

polarograph	2-methylindole
3.1 ppm	3.2 ppm
3.0	
3.0	
2.8	
2.8	
2.7	

On another sample of monomer that had been reported "less than 1 ppm aldehyde" we found 0.7 and 0.7 ppm on duplicate samples.

Since the polarographic method has been used only when there has been some confusion about the results obtained by our lab and those reported by one of our suppliers, we are at present somewhat flummoxed as to just what the accuracy of the method is. For an example, here is an interesting case.

Our supplier reported 11.8 ppm aldehyde on a tank car --- only to rescind that figure for 5.6 ppm. The shifts found 8 to 10 ppm on this car. The polarograph found 11.2 and 11.2 ppm.

On the second car taken from the same storage tank the supplier stuck to his 5.6 ppm figure. The shifts found 6.9 and 6.9 ppm. The polarograph found 11.2 and 11.0 ppm. What to believe?

Some more results.

	polarograph	2-methylindole
Sample 1	8.2 8.5 8.5	7.2 6.3
Sample 2	5.7 5.5	6.9
Sample 3	8.5 8.1	10.6 over 10
Sample 4	19.3	14.0
Sample 5	0.8	less than 1
Sample 6	1.3	less than 1
Sample 7	11.6 11.6	8.0

That's about it, Lou. We'll get the shifts to run both methods so we can gather more detailed information. We also might obtain some small, weighable sample bombs and bubble the monomer directly into the polarographic cell.

Before closing it probably should be mentioned that we did investigate the effect of the nitrogen purge --- and we did investigate to see how well the aldehydes were entrapped in the buffer solution.

Thanks for your interest, Lou. We would appreciate any comments or suggestions you might care to make.

JP:mja
Attachments
cc: H. L. Siegmann
A. H. Taylor

W. J. PARKER

C. A. Wamser
R. A. Wilson

Cumberland

R. A. Wilson (2)
Calvert City

R. L. Siegmann
Calvert City

10/25/60

VINYL CHLORIDE RUN DOWN TANK ANALYSES

Attached are typical run down analyses for the various periods of operation as requested by you. There are, of course, many more such analyses available, but they do not differ significantly from those listed.

R. L. SIEGMANN

RLS:mja

Attachment

cc: 1. C. R. Wagner
2. J. W. Frevert
3. R. F. Gasaway

TYPICAL VINYL CHLORIDE RUN DOWN TANK ANALYSES

	parts per million								
Date	Aldehyde	C_2H_2	Iron	H_2O	HCl	Non-vol	°C. Dorell	%Conv.	Resin Viscosit
2-20-60	3.4	0.8	nil	220	8	59	0.4	75.7	2.53
2-26-60	4.7	nil	0.4	480	4.0	97	0.15	85.0	2.86
3-1-60	nil	nil	nil	140	1.9	7	0.15	90.0	2.99
3-5-60	nil	nil	nil	269	0.7	8	0.35	90.0	2.97
3-15-60	1.3	nil	0.1	264	4.9	28	0.2	91.5	2.93
4-5-60	6.6	nil	nil	314	4.5	22	0.15	92.4	2.92
5-14-60	nil	nil	nil	613	nil	67	0.1	94.0	2.84
5-17-60	nil	nil	0.2	975	3.6	141	0.1	98.0	2.67
6-13-60	nil	0.5	nil	664	1.0	58	0.2	93.0	2.88
6-15-60	<5	2	nil	677	6.0	201	0.1	94.0	2.82
6-20-60	1.0	nil	nil	434	nil	83	0.2	87.0	3.05
7-1-60	<5	0.8	0.01	1035	nil	68	0.1	93.0	2.89
7-6-60	<5	0.8	nil	792	0.8	100	0.2	93.5	2.92
7-17-60	<5	nil	nil	789	2.9	20	0.15	91.5	3.15
8-27-60	1.8	2.8	1.7	929	nil	45	0.1	94.0	2.78
8-31-60	0.6	nil	nil	872	4.9	18	0.05	96.5	2.71
9-5-60	0.9	nil	nil	583	1.7	34	0.2	97.0	2.90
9-20-60	<1	nil	nil	646	nil	34	0.2	96.0	2.80
9-24-60	nil	nil	nil	448	nil	40	0.2	96.0	2.68
9-24-60	nil	nil	nil	573	nil	302	0.15	96.0	3.22
9-28-60	nil	nil	nil	977	3.2	60	0.15	95.3	2.74
10-2-60	nil	nil	nil	933	3.2	476	0.2	97.0	2.67
10-6-60	nil	nil	nil	637	nil	9	0.2	96.6	2.73
10-7-60	nil	nil	0.6	770	nil	24	0.2	97.7	2.75
10-9-60	nil	1.6	nil	324	nil	22	0.2	97.5	2.73
10-12-60	1.25	nil	nil	528	nil	19	0.2	97.9	2.55

10-17-60	nil	nil	nil	260	nil	112	0.3	96.0	2.62
10-18-60	nil	nil	nil	375	nil	12	0.2	82.3	2.91
10-20-60	nil	nil	nil	303	nil	53	0.2	89.3	3.05
10-23-60	3	nil	nil	86	nil	294	0.2	95.5	3.17