

J. D. Fannin	FIELD POINT OR DEPT. & BLDG. NO. Louisville	25-1755	DATE THIS LETTER
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SUBJECT

Louisville's Vinyl Chloride Personnel Monitoring Program

Thank you for the opportunity to visit the Louisville plant and examine in depth the personnel monitoring program for vinyl chloride. Your dual tube program to determine the incidence of vinyl chloride breakthrough has shown that vinyl chloride is breaking through the primary tube about 30% of the time. However, after close examination of your measurements, it is clear that only 13% of the time is this breakthrough greater than 35% of the amount retained on the primary tube. I judge this situation as serious and in need of explanation and correction but not critical.

The cause of the breakthrough is not clear to me. It can be related to poor sampling practice, dirty PMCC tubes (inadequately cleaned) and excessive amounts of water on the PMCC tubes. It is likely that all of these contribute to the problem. It is my judgement that thermal cleaning is a small factor. It is more likely that unusually large quantities of water are responsible for the breakthrough. Unusually large quantities of water are those which arise from collecting suspended water (fog and mists) not just the water from humidity conditions.

- PMCC dual tube program from February 1976 through July 1976 generated 215 sets of measurements (2 tube combinations). This represents 9% of the 2524 personnel monitorings conducted during that period. The program shows that in 63 cases (29%) of the 215 dual tube tests breakthrough greater than 10% occurred. These breakthroughs are not related to the amount of vinyl chloride retained. My calculations show the following distribution among the 63 breakthrough cases;

PPM Range	Percent of the 63 Breakthrough Incidents
<.1	11
.1 to .43	14
.44 to .86	24
.87 to 1.63	22
1.64 to 3.26	19
>3.27	10

Two qualifications need to be imposed upon your results to bring them into proper perspective. First of all, the number of breakthroughs (63) should be reduced to 55 based upon a probable artifact of dual tube programs. Eight dual tube sets showed virtually nothing in the primary tube and all of the measured vinyl chloride in the secondary or back up tube. It seems that the tubes were reversed and the primary was sampled, labeled or analyzed as the secondary and vice versa.

Then, we must not use 10% breakthrough to the secondary as significant but rather choose 35%. When we use this new criteria we see that 13.5% of the 215 tests showed breakthrough. This says that 13.5% of the time single tube personnel monitors will be out of the $\pm 35\%$ accuracy interval identified by OSHA for measurements in the range 0.5 to 1.0 ppm. In other words one out of every 10 personnel monitorings is a bad test but which one is it? It is safe to assume that if we can find the reason for this breakthrough we can reduce this uncertainty.

examined your personnel monitor program in further depth, looking at the laboratory's work, the calibration of the pumps by your people, the selection of the test subjects, the circumstances of actual field sampling (the incidents of the six hour sampling period) and the storage of the PMCC's before and after sampling. Based upon my examination I make the following comments:

- a) Proper care is made to calibrate PM pumps prior to and following the six hour sampling period.
- b) Good attention is given to the selection of employees to be tested.
- c) Inadequate attention is paid to observing the employee, his pump and tube during the six hour sampling period.
- d) Insufficient attention is paid to the water "puffing" during the analysis of PMCC's. When water "puffing" is observed the measurement should be voided.
- e) The laboratory needs to analyze freshly cleaned PMCC tubes (~20) to determine the average signal level from cleaned tubes. Then subtract out this value as a "blank".

I took the time to observe personnel samplings which were in progress. I found a sampling which was subjected to massive water sprays and mists. This water can be retained on the PMCC tube. I found a case when the pump and tube were resting on the window sill with no one around. Finally, in a spot check for the men and pumps of 10 samplings I could find only 2 tests. Not knowing where the others are, what they may be picking up or if they are in use is a serious question. It is a good idea to pay closer attention and record the conditions during the six hour sampling.

The incidence of water "puffing" was observed in the lab and I feel it tells us that a great deal of water (too much) is on the PMCC tube. When the tube is removed from the Bendix Flasher after analysis, a puff of steam jets up from the point where the tube seats in the downstream solenoid. In addition to that, occasionally water is so abundant that it collects in the connecting tube between the flasher and chromatograph. This is concluded from observations of water puffing following the second, third and fourth triggering of the flasher inject switch after the first "puff" is observed and before any PMCC tube is installed in the flasher. At present this puffing observation is not even recorded. It should be recorded and it should be the basis of voiding a measurement.

It is a good idea to continue the present dual tube runs employing new PMCC tubes and 300°C cleaning. Fifty or so tubes seem adequate to establish if 300°C cleaning will eliminate the breakthrough observed from December to July.

It does not seem likely that this will eliminate the breakthrough because breakthrough is not primarily associated with low level samples.

It is clear from humidity studies at Brecksville that humidity up to 92% (relative) does not alter the performance of PMCC's or produce significant breakthrough. There is, however, the likelihood that water in droplet form (fog, mist) can be filtered by the PMCC thus depositing quantities of water much greater than that resulting from 92% relative humidity

ir. This very large quantity of water could easily account for breakthrough. It should also be associated with the water puffing observed in the laboratory.

In the light of suspected high water charges to the PMCC your proposal to try a desiccant study is wise. I have two recommendations for desiccants, silica gel and calcium hydride.

The silica gel recommendation comes from work Chuck Titus completed. In testing a vinyl chloride point source for composition, a silica gel trap was placed upstream of a carbon trap. Vinyl chloride and other monomers were transmitted by the silica gel but water was retained. We do not know if this case was 100% transmission of vinyl chloride through the silica gel. However, analysis of the silica gel should clear up this point. And I would analyze the silica gel with the carbon disulfide procedure just as if it was carbon. The basis of this silica gel recommendation is a mass spectroscopic analysis of the carbon bed which was performed for Chuck by Bob Lattimer of the Brecksville lab.

The calcium hydride recommendation comes from work being carried out by John Nikora at the Avon Lake Development Center. John is using a calcium hydride tube ahead of a carbon tube in a gas stream. The stream purges a water sample (and thus becomes virtually saturated with water) to strip vinyl chloride from the water. The calcium hydride removes the water but does not appear to retain the vinyl chloride which is retained on the carbon bed. This is a preliminary conclusion because the calcium hydride bed has not been analyzed for retained vinyl chloride. John has only prepared various mixtures of VCl and water (at the part per billion level) and obtained good straight line relationships between analyses and VCl content. You can get more details and keep up to date on this work by discussing the work with John at Ext. 288, Avon Lake Development Center.

summary, I believe you have a breakthrough problem which is serious but not critical. I do not know if this same problem exists at the other PVC production facilities but I will find out. I recommend you continue your breakthrough program with 50 sets using new and clean flasher tubes and 50 tests employing desiccant tubes. You and the other plants will be receiving the PMCC/humidity report from Brecksville. Finally, I plan to examine all BFG data and experiments and prepare the best statement of accuracy and uncertainty relating to personnel measurements employing the PMCC/flasher method.



Paul M. Zakriski

jb

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