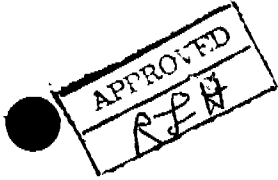


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Meeting on Vinyl Chloride Analytical Methodology

October 31, 1975

Attendees

Mr. Hubert Lawes, ICI Plastics
Mr. William Thain, British Petroleum
Mr. George Lyles, Kem-Tech Laboratories, Baton Rouge
Mr. H. E. Broemmelsiek, Tech Services
Mr. B. M. O'Rear, Plastics Applications
Mr. D. Watts, Ind. Hygiene
Mr. G. C. Gaeke, R&D Services

Introduction

Mr. Lawes and Mr. Thain are visiting this country as representatives of Chemical Industries Association (CIA,UK) Vinyl Chloride Analytical and Monitoring Committee. Mr. Lawes contacted Dr. A. J. Haefner concerning a meeting with Ethyl and other local companies involved in vinyl chloride analytical methodology in this area. Representatives of Dow Chemical and Georgia-Pacific were invited to the meeting but did not attend.

Mr. Lawes briefly discussed the CIA,UK Committee on Vinyl Chloride. There are actually four groups which make up this committee. One is concerned with medical problems and issues; one with plant practice and process improvements (VCl and PVC); the third with customer (small fabricators) problems; and the fourth with analytical methodology. The committee is recognized by the British government as a group of experts in the area and accepts the committee's advice in regard to levels in the work place atmosphere and analytical methodology. The committee is also working with similar organizations in the Common Market countries in an effort to obtain common standards and analytical methods throughout Europe. As an example of the problems involved in obtaining common standards, Mr. Lawes quoted the following standards as existing in Europe today: U.K., 10 ppm TWA, 30 ppm ceiling; Germany, 5 ppm (1 year TWA); Belgium, 25 ppm; Denmark, 100 ppm; France, 10 ppm; Italy, 25 ppm; Russia, 11.5 ppm; Sweden, 1 ppm; Switzerland, 100 ppm.

As an example of the type of documents issued by the CIA, UK; Mr. Lawes showed us a copy of the "Chemical Industries Association Analytical Manual - The Determination of Vinyl Chloride", 2nd ed. (Ethyl has a copy of the 1st ed.) and also showed us a draft copy of a memo (copy attached) on the control of vinyl

chloride in foodstuffs in which the committee recommends to the government a level of 50 ppb as acceptable in foods.

Discussion

The discussion covered the following broad areas of analytical methodology: environmental testing, personnel and fixed point monitoring, leak testing, PVC slurries, and foods.

In the area of environmental testing, Mr. Thain pointed out that the goal in England is a 24 hr sample with a limit of detection of 0.01 ppm VCl. They have been using a charcoal tube (1.2 g charcoal) with an air sample rate of 20 ml/min for 24 hrs (288 liters). They have recently recognized that the sample size is too large (moisture desorption effect). They have found that the moisture effect can be eliminated by the use of a $MgClO_4$ dryer ahead of the charcoal tube (the $MgClO_4$ does not adsorb VCl). They also have been using the UEI (MDA in this country) color tape sampler for environmental testing. They noted that this instrument appears to produce a positive and erratic blank (0.04 - 0.08 ppm VCl) and therefore do not feel that it is suitable for VCl levels below 0.1 ppm VCl. We indicated that Ethyl has done very little in the area of 24 hr. ambient level sampling. Mr. Lyles (Kem-Tech) also said that they have not done very much work in the area of 24 hr sampling. We briefly discussed the EPA procedure for ambient air (1 g charcoal, 200 ml/min) and everyone agreed that the method is essentially worthless (Mr. Lawes and Mr. Thain had visited EPA the day before their visit to Ethyl). The idea of charcoal adsorption followed by thermal desorption was briefly discussed as a possible method for ambient air monitoring. Our experience with the Bendix Flasher was discussed and Mr. Thain discussed the approach that B.P. has been following. He noted that charcoal containing iron catalyzes the cracking of VCl to ethylene in the thermal desorption step. He also indicated that they have recently been working with a special carbon (Sutcliffe Speakman 607C carbon) which they have found to be very good in moderate humidity atmospheres - 0.5 g of carbon at a flow of 10 ml/min is good for 29 hrs of sampling! They will continue their research on this new carbon (it is not available commercially at the present time) but they feel that it may be the answer to the 24 hr sample problem.

In the area of personnel monitoring we described the system we are presently using and the ASTM proposed method (both based on charcoal adsorption, CS_2 desorption, gas chromatography). They use a similar procedure (10 g charcoal, 1 l/min flow, methylene chloride desorption, gas chromatography). They have also used the Sipin pump in some studies with lower flow rates and smaller amounts of charcoal. ICI has been very active in the development of a paper tape personnel monitor similar to the MDA unit (oxidation of VCl to Cl_2 and reaction to produce a colored stain on a moving paper tape). Mr. Lawes reported that they have developed a unit much smaller than the MDA unit presently available

based on this principle. The ICI unit will be commercialized and should be on the market approximately by mid 1976.

For fixed area monitoring, the British industries are using systems similar to those available in the U.S. i.e. either Miran II infra-red instruments or gas chromatographs. In answer to a specific question concerning maintenance both Mr. Lawes and Mr. Thain indicated that wage-roll personnel were used for all routine service but that special training programs on instrument maintenance were required for the gas chromatographs. Sample points for the fixed area instruments are selected to cover two major areas: (1) where maximum values are likely to occur and (2) where potential leaks are likely to occur.

For the determination of VCl in PVC resins and slurries the Perkin-Elmer Model F-40 headspace analyzer is used in England. We indicated that we are using the same instrument for resins and will be using the instrumentation for slurry analysis in the near future. I indicated that I would send them a copy of our headspace procedure for VCl in PVC resins and compounds since it is slightly different from the CIA,UK procedure.

In the area of leak testing, the English industries are using the Century portable FID instrument as we are. Mr. Lawes indicated that ICI has been evaluating the h Nu photo-ionization instrument but have had some problems with calibration. We mentioned that we have also used the Miran I infra-red instrument for leak testing.

In the area of food analysis, the English industries are using headspace analysis to determine VCl concentration down to about 50 ppb. I discussed the recent FDA proposals and indicated that we were able to determine ~1 ppb in water and 3 ppb in 50% ethanol. They expressed a real interest in this procedure. Again they mentioned the efforts being made to develop a standard that would be suitable for the Common Market. They indicated the following present limits in Europe: Germany, 1 mg VCl/kg food intake/day; Holland, migration limit of $<50 \mu\text{g VCl}/6 \text{ dcm}^2$ of PVC surface; France, 50 ppb in food (France packages wine and water in PVC containers); Italy, not detected by standard method (limit of detection 0.05 ppm); England, no standard at present but probably 50 ppb. Both Mr. Lawes and Mr. Thain believed that the final European standard would be based on VCl content of PVC rather than VCl content of food.

In summary, Mr. Lawes and Mr. Thain were very open and frank in their discussions concerning analytical methodology adopted by the CIA,UK VCl Committee and were equally frank in their discussions of new methods currently being evaluated. They indicated also that they had gained considerable knowledge concerning Ethyl's analytical methodology. It was generally concluded that a mutual exchange of ideas such as took place

at this meeting was what they had hoped to obtain during their visit to this country.

G. C. Gaeke
Sr. Research Associate

GCG:wj

Attach.