PROGRESS REPORT

JUNE, 1974

Analytical, Flammability, On-Line
Instrumentation & Physical Testing Groups

L. B. Crider

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Code Zero Activities - L. B. Crider

1. Analyses of perimeter air samples taken at distances up to 3 miles from the Avon Lake General Chemical Plant showed VCM concentrations in the range of 0-176 ppb. This first set of 26 samples were collected at locations and at frequencies derived from the modified EPA method. A statistical analysis of these data has lead to the recommendation that two additional sets of similar data be collected to provide an adequate data base to develop a sampling model for our other production plants. This additional sampling and analyses are scheduled to be completed the first week in July.

2. A gas chromatographic method based on flame ionization detection has been developed for detecting VCM in ambient air samples at the 1 ppb level. The basic principle involves the adsorption of a 250 cc air sample on activated charcoal contained in the sample loop of a gas chromatograph. The VCM is then thermally desorbed in the GC. A calibration curve has been obtained covering the range of 5 to 280 ppb. At the 20 ppb level a 9% deviation in reproducibility was found.

3. To provide the necessary instrumental systems that may be required to meet future OSHA criteria for monitoring VCM levels below 10 ppm we have established a new set of objectives for the AVCM Task Group to rapidly identify and field test new monitoring systems. In general, this new system must be specific for VCM in the range of 0.1 - 10.0 ppm; be continuous or rapid sequential in monitoring operation; be inexpensive, easy to operate, have low maintenance requirements; and it must be compatible with our present Bendix sampling systems. The methodology that we will apply in meeting these objectives are essentially the same as in our previous task group function, i.e., make a survey of available methods; select the best candidates for laboratory and field testing; install and operate a prototype system; compare the performance with our present Bendix System.

4. An EA has been approved to fund the PVC degradation study at the University of Akron. This work, under Dr. Paul Garn will be directed toward a definition of VCM (if any) produced at processing temperatures. Work on this project will begin about mid-July.

NMR and Mass Spectroscopy - J. L. Dorsch

1. Support of Code Zero work consumed about 95% of our effort this month. We are continuing to determine ambient vinyl chloride monomer (AVCM) in air samples taken at our PVC customers' plants. The concentrations found have been 1 ppm or less in most samples except ones taken in PVC storage containers (railroad cars, tanks, bins, etc.) or taken in the exhaust gases of mixers or extruders.

2. We have begun Phase 1 of the AVCM perimeter monitoring program for our PVC plants using the method developed by O'Mara and Quisenberry. Phase 1 will be the analysis of four air samples taken from each plant perimeter. We hope to shift the analytical work for Phase 2 to the plant laboratories.

NMR and Mass Spectroscopy - J. L. Dorsch (cont.)

3. A program to develop a G.C. method for analyzing air samples from the Hydrin semi-works plant has been initiated. Our goal is to determine epichlorohydrin and other toxic molecules in air at the ppm level. It seems likely that we will eventually have to determine these molecules at the ppb level miles from the plant as we are now required to do for vinyl chloride. Bill Williams, Jr., a summer technical employee assigned to the Hydrin Group, will assist us in this effort.

4. During the period May 20-22, I attended a workshop sponsored by Varian Associates and CWRU on carbon-13 nuclear magnetic resonance spectroscopy. It is now obvious that the application of Fourier Transform methods to NMR, which made possible routine observation of carbon-13 spectra, was the most important analytical development of the past decade. With reliable, powerful instruments now in the vicinity of $60,000, it will not be long before we will be able to justify the expense for our own work. A critical need at the Technical Center is for better methods of identifying the impurities in polymer chemicals. Carbon-13 NMR will be very useful because every carbon atom in the molecule will be observable. With our present NMR instrument, we can observe only hydrogen atoms. Structures which contain no hydrogen atoms such as isocyanurate rings as in Good-rite 3125, and di thio carbamates as in curing agents and accelerators, are invisible to H NMR spectroscopy.

On-Line Instrumentation - L. W. Salzer

1. A process chromatograph for the measurement of VCl and VCl_2 has been ordered from Bendix Instruments. This instrument is to be installed in Bldg. 464 at ALGCP. Results obtained from this chromatograph will be compared to the results presently being obtained from the Total Hydrocarbon Analyzer. It will analyze six sample points and the same sampling system will be used for both instruments. A few modifications of the present sampling system are necessary in order to accommodate both instruments. We expect delivery of this chromatograph early in July.

2. Reports on the Total Hydrocarbon Analyzers installed and in operation at all Poly buildings in the company remain good. The instruments have been in operatin for many months and maintenance is very low. As of now the writer knows of no malfunctioning instruments. The level of total hydrocarbons is decreasing weekly and good maintenance and improved operation of the poly plants is noticeable.

3. A visit was made to Calvert City for the purpose of seeing their on-line process instruments and the instrumentation being used in air monitoring work. The trip was interesting and beneficial. Calvert has a chromatograph analyzing air samples from the North Synthesis Unit. The instrument is analyzing ten streams for six components. The time of analysis for each stream is 16 minutes. Of the components measured EDC had the highest concentration of all.

Atomic Absorption - Estelle Truscott

1. In May, 1973, the National Sanitation Foundation changed their analytical procedure for tin to determine whether the water extract exceeded the limit of 50 ppb. Hi-temp (CPVC) does not pass the tin extraction requirements. Thus, extraction studies with CPVC are being done by A. P. Metzger. I have set up our AA instrument to analyze these extracts by the NSF analytical procedure. The new tin electrodeless discharge lamp, which is more stable than the hollow cathode lamp, was purchased. The analyses of these extracts seem to indicate extrusion temperature affects the level of tin in the water extract. Some of the extracts are being analyzed by three different laboratories to obtain information as to the reliability of the analysis at the level of 50 ppb. I am investigating the possible use of the furnace, a flameless technique, in conjunction with the tin EDL to measure low concentrations of tin. I have found that 20 ppb can be measured accurately. However, the tin extracts from the pipe have presented problems, which I have yet to solve.

2. Seven samples of zinc oxide were sent from the laboratory of the Akron Tire Plant and Industrial Products. A request was made that the lead content be determined by atomic absorption. The levels analyzed were from 0.1% to 4.8%. This work was requested in order to determine specifications for the zinc oxide being purchased. An analytical procedure was developed for AA for them to use when they get their AA instrument operating.

3. A literature search was done to determine what had been reported regarding the vinyl chloride content of automobile exhaust. It was thought that the ethylene dichloride, the lead scavenger added to gasoline, would under combustion conditions produce HCl and VCl. No references in the literature were found to support this thought.

X-Ray Spectroscopy - R. A. Yount

1. An x-ray diffraction study has been made to determine whether relative crystallinity of Epcar-Polypropylene blends can be used to determine the physical properties. The method seems to be unsuitable for this application. We have found that the results cannot be duplicated because the polymer samples are not homogeneous. The X-ray beam width is narrow, consequently the sampling volume is small and any variation in the polymer blends gives gross differences in results.

2. The use of cerium naphthanate as an internal standard for measuring the oil content of oil extended Epcar was not successful. The naphthanate does not stay in solution with the oil. Rather than spend any more time on cerium, other candidate materials are being sought and will be evaluated as soon as they are received.

3. Continued surveillance is being made of the oxyhydrochlorination catalyst for the international licensing program of the vinyl monomers group. We are training one of their people to make the x-ray measurements so that I might be free to spend more time on other problems.

X-Ray Spectroscopy - R. A. Yount (cont.)

4. We have started the surveillance of the catoxid catalyst also for the international licensing program. X-ray analysis is used to determine the silica content. The optimum silica content is 6%. The x-ray method is very rapid as compared to the wet methods currently used so this should be a real aid to the monomers group.

Liquid Chromatography - Peter Dmyterko

1. Studies are being conducted by the antioxidant group to improve the crude MBT (2-mercaptobenzo-thiazol) reaction by a better purification procedure and recycling the tarry residues. A sample of the MBT tars was analyzed on a Zorbax Sil column with the result that three major impurities and 15 minor impurities were observed. Attempts will be made to identify the major components.

2. Several additional columns were evaluated in an effort to improve our present NMA (N-methyloacrylamide) analysis. These included polyamide, cationic exchange and anionic exchange columns. However, the resolutinn on these columns was not better than that of our present ETh (ether type) column.

3. Studies are being conducted to determine the levels of Tinuvin P (2[2' hydroxyl 5' methyl phenyl] benzothiazol) and Irganox 1010 (tetrakis [methylene 3(3'5' di t butyl -4' hydroxyphenyl) propionate] methane) in polyurethanes after processing. A liquid chromatography procedure for measuring the levels of these components in extracts of the polymers after processing is being developed.

4. Several of the new Perkin Elmer Silx type columns are being evaluated. These columns are cheaper than our present 3 meter columns and appear to have comparable resolution on many analyses.

Physical Testing - Frank Baron

1. The conversion of an NBS Mooney Machine from 2 RPM to 0.5 RPM has been completed and test data has been supplied to N. Nakajima.

2. We have extended the burn cycle of the Weather Ometer carbons from 16 hrs. per day to 18 hrs./day. This will result in a terrific cost savings over the ensuing years.

3. The Plasticorder area has been painted.

4. Jeannette Woolsey has been assigned part time work from this department.

5. We are continuing to accept contract bids for pipe testing from suppliers.

Physical Testing - Frank Baron

6. Dale Butcher has been asked to fill in as the need arises in the Analytical Lab.

7. Transferred Rheovibron Tester to the Physical Test Area.

Gas Chromatography - E. G. DeCapita

1. HP Model 5711A gas chromatographs with integrating computors have been installed in the Louisville, Long Beach and Pedricktown plants. They are equipped with the necessary valves and columns for the back-flush technique for analysis of RVCM in resins and compounds. They are also equipped with a second column for RVCM in slurries. Visits were made to the three plants to instruct personnel in performing the analyses. All of the production plants and ALTC labs now have the same type chromatograph in use for RVCM analyses. Analyses are now being performed on a routine basis in all these laboratories.

2. At their request, I have supplied the Niagara Falls, Ontario plant with information about the equipment they will need to duplicate our procedures for RVCM analyses. Present indications are that they plan to purchase the necessary equipment. A price quote from Hewlett-Packard is being sent to them.

3. Three samples of Methoxy Ethyl Acrylate (MEA) were analysed. One of them was causing a difference in Tg between rubber made in lab equipment as compared to process equipment. The MEA used in the process contained about 19% of some unidentified impurity. It was decided to discard the process MEA.

4. All other analyses performed were Code Zero related. These included analyses of cap liner and flex hose compounds from the Marietta Plant, resin and water from HOCl treated materials, variously treated 103EPF76 and 222 resins, latex samples, and Cepacol.

Absorption Spectroscopy - J. W. Ryan

1. I have examined several samples related to the Geon build-up problem. One was a water phase polymer of low conversion. This showed a carbonyl absorption in addition to PVC absorptions. Actual build-up specimens have also been examined. Both attenuated total reflection (ATR), a surface phenomenon, and specular reflectance, a transmission technique, have been applied. Specular reflectance is a new technique and, as yet, an unfamiliar technique. Reflector plates with build-up have been extracted with tetrahydrofuran to remove PVC. The plates have been subjected to more build-up to develop a layer of initial material thick enough to scan and be able to determine its composition.

Absorption Spectroscopy - J. W. Ryan (cont.)

2. We have calibrated the Miran Gas Analyser for epichlorohydrin (ECH) at two wavelengths and have prepared calibration curves for toluene and heptane at one wavelength each. ECH was monitored for an 8 hr. period on the 2nd and 3rd floors of Bldg. 417. Hydrin levels are estimated at near the OSHA limit. We need gas chromatographic confirmation before releasing the values. Some interference may be present.

3. Mike Mohler, a summer student, is developing isocyanate analyses for our use. He has calibration data for Hylene-W in the atmosphere and is now working on a calibration of MDI in the atmosphere.

4. Infrared spectra were prepared for several samples of chemically modified polyacrylic acid. The spectra confirmed the reaction and indicated the degree of completeness.