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APPENDIX I

CONTINENTAL OIL COMPANY

RESEARCH AND DEVELOPMENT DEPARTMENT

5, 22

ANALYTICAL RESEARCH SECTION

RESEARCH SERVICES DIVISION

TECHNICAL SERVICE REPORT

NO. 460-74-838-1  
October 28, 1974

ADDRESS INQUIRY TO:

F. Kennedy

TO: Dr. Flynt Kennedy

SUBJECT: AIR MONITORING FOR VCM

SUMMARY:

At this point in time there appear to be two methods deemed adequate for monitoring ambient air for vinyl chloride monomer (VCM): (1) charcoal adsorption and (2) air bags, bottles or some type of container for spot monitoring. Both methods use gas-liquid chromatography as the final analysis to detect and quantitate the VCM. The charcoal adsorption technique basically involves pulling the ambient air through a bed of charcoal using some suitable pump. The charcoal adsorbs the VCM. The air is pulled through the bed at a fixed pumping rate for a fixed time period. The VCM is then desorbed from the charcoal using a known amount of suitable solvent (generally carbon disulfide). The resultant eluant is chromatographed using gas-liquid chromatography and the VCM detected and quantitated. The air bag method utilizes an impervious bag into which the ambient air is pumped. The resultant air sample is chromatographed using gas-liquid chromatography and the VCM detected and quantitated against a known mixture of air/VCM. The ease of the latter method as well as the ability to reproduce samples accurately has dictated its use within our plants.

DISCUSSION:

Both methods of air monitoring described in the summary have been evaluated in our laboratories. The carbon adsorption technique is fraught with numerous problems, one of which is the difficulty in obtaining adequate accuracy and precision at the one-part-per-million (ppm) level, now advocated to be the standard as of 1/1/75. For this and various other reasons, we have discarded the carbon adsorption technique in favor of air bag sampling and I will confine my remarks to this technique as the one of choice within Continental Oil Company. However, several independent laboratories still use carbon adsorption and, when using such laboratories, I think it mandatory that the customer insist on proof of adequate precision and accuracy to meet the new permanent standard.

In our facilities we utilize an air bag made from laminated polyester obtained from Calibrated Instruments, Inc., 731 Saw Mill River Road, Ardsley, New York 10502 (Tel. 914-693-9232). They stock various sizes; the one of greatest popularity within Continental is the 7-liter size. Various pumps can be used ranging in price from \$3.95 to \$350. We have evaluated three different pumps: (1) NAPCO, which is an aerator pump for minnow buckets. It costs \$3.95, runs from a single "D" cell battery, and can be found at most sporting goods stores. (2) Lew's air pump--another minnow bucket aerator pump, runs from two "D" cell batteries, costs \$7.95,

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and can be found at most sporting goods stores. (3) Sipin--a specially designed pump for use with charcoal tubes with built-in volume counter and pumping rate adjust; can be purchased from the Anitole Sipin Company at a cost of \$350. The Sipin pump appears to give no better pumping rate or consistency than either of the other two. All appear to give a representative sample.

When using the air-bag-sampling system with either of the cheaper pumps, a Hoke needle valve is inserted in the intake line to adjust pumping rate. At full pumping rate both pumps pump at approximately one liter per minute, which means the bags will be full in seven minutes. Both pumps are capable of bursting the bags, so the bags should not be overfilled. The restrictor valve can be adjusted to produce the desired flow rate without impairment of the pump. A simple harness can be constructed from webbing straps to fit over the shoulders of an individual. The bag is taped to the harness and rests on the worker's back. The pump is either taped to the harness on the front near the breathing zone or a pocket can be fabricated that the pump will slide into. A rubber hose is connected from the pump outlet to the bag via the restrictor. The bags have on-off valves which can be closed when the bag is full to preclude loss when the hose is disconnected. When the bag is near full, the valve is closed, the bag taken to the laboratory and the contents analyzed. The bag should be kneaded several times to insure complete mixing. A five-milliliter sample is withdrawn with a syringe and one milliliter of this gas injected into a gas chromatograph equipped with a flame ionization detector and an appropriate column. The choice of column is generally dictated by other species in the air besides VCM. The column must be capable of separating these components from VCM so they do not interfere with quantitation. An example of instrument and column is a Carle Model 9500 flame ionization chromatograph equipped with a gas sampling and backflush valve. The column is a 6' x 1/8" O.D. aluminum tube packed with 80/100 mesh Chromosorb 101. The chromatograph is from Carle Instruments, 1141 East Ash Avenue, Fullerton, California 92631. They will furnish the column on request. Identification of VCM is made from relative retention times and quantitation is accomplished by comparison with a known standard of VCM. Standard samples can be obtained from Precision Gas Products, Inc., 681 Mill Street, Rahway, New Jersey. A size 16 cylinder of 1.0-, 25-, or 100-ppm standard will cost approximately \$100. The validity of the standards is good for approximately three months after which time the VCM content will appear low. The analysis takes approximately five minutes. If precision data are desired, several samples can be analyzed from the same air bag. Once the analysis is completed, the bag is evacuated, filled with VCM-free air or nitrogen, re-evacuated, and this process continued for at least three times. The bags are then ready for use again. Memory effects from VCM are essentially nil if this procedure is followed. Detection limits are of the order of 0.1 ppm. For eight-hour time-weighted averages, it is suggested the bags be filled in four-hour increments and the results time-weighted for eight hours. A single eight-hour run may require severe enough restrictions on pumping rate so as to cause erratic pumping and a nonrepresentative sample.

The above procedure has been successfully used throughout Continental's plants and laboratories. If a given plant is not equipped with a suitable chromatograph, the sample can be shipped to an independent laboratory for analysis. Another alternative is to allow an independent laboratory to both sample and analyze for a given plant. The methods employed by independent laboratories will vary, and I strongly suggest that when this approach is utilized, the laboratory contracted supply adequate proof as to precision and accuracy of their results. Some of the laboratories which provide this service are:

1. Dow Chemical  
Midland, Michigan 48640  
Tel. (577) 636-5314

They use charcoal adsorption and charge \$45/hour, and it takes one hour/sample.

2. Arro Laboratories  
Joliet, Illinois  
Tel. (815) 727-5436

They request samples in glass bombs and use mass spectrometry for analysis. They claim parts-per-billion sensitivity. They give one-week turnaround on samples. Their charge is \$60/sample for 10 samples or less and \$50/sample for over 10 samples.

3. Stewart Laboratories, Inc.  
820 Tulip Avenue  
Knoxville, Tennessee 37921  
Tel. (615) 525-1123

Unknown as to how they sample or analyze.

4. Denver Research Institute  
Denver, Colorado  
Tel. 753-2911

Charcoal adsorption, but do not furnish the tubes. Approximately one week turnaround. Present charge is \$25/sample, but negotiable, depending on number of samples.

5. G. D. Clayton and Associates  
25711 Southfield Road  
Southfield, Michigan 48075  
Tel. (313) 424-8860

Charcoal adsorption - they furnish the tubes. They charge \$10/sample plus \$1/tube.

6. Chrometrics Laboratory, Inc.  
808 Busse Highway  
Park Ridge, Illinois 60068  
Tel. (312) 696-3036

They use evacuated canisters. They furnish the canister, you take the sample and mail the canister to them for analysis. They claim 0.1 ppm sensitivity to VCM. Approximately 72-hour turnaround. They charge \$15/sample, including canister, return mail costs and a quantitative analytical report.

This list is not complete, but gives an idea of where and how such analyses can be obtained. I take no responsibility for the laboratories mentioned as to their ethics or abilities.

  
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Analytical Research Section