Methods for atmospheric vinyl chloride measurement have been reviewed. The lowest detection limits and most specific measurement are achieved by scrubbing atmospheric samples with activated charcoal, desorbing the vinyl chloride, and assaying it by gas chromatography (GC). NIOSH currently recommends collecting samples using tubes packed with 150 mg of coconut shell charcoal, desorbing with carbon disulfide, and analyzing by GC equipped with flame-ionization detection (FID); the method is capable of detecting less than 1 ppm vinyl chloride and has an apparent recovery of about 90%. With thermal desorption techniques, the detection limit can be reduced to the ppb level with no loss of accuracy or precision. Some field methods, such as infrared analysis and conductivity measurement, are capable of detecting 1 ppm or lower but are subject to interferences by other contaminants; they could be useful for evaluating sources of vinyl chloride leaks and for continuous monitoring. Permeation tubes are superior to gravimetric or volumetric methods for generating atmospheres of known vinyl chloride concentration.

Measurement of atmospheric vinyl chloride

SHELDON S. LANDE
Center for Chemical Hazard Assessment, Syracuse Research Corporation, Merrill Lane, Syracuse, NY 13210

introduction

Occupational exposure to vinyl chloride has often resulted in a comprehensive syndrome which is now termed as "vinyl chloride disease." Prolonged exposure ultimately ends in fatal hepatic angiosarcoma.[1] The chief commercial use for vinyl chloride is the production of polyvinyl chloride. Until occupational exposure studies traced a high incidence of hepatic angiosarcoma among vinyl chloride polymerization workers, its occupational standard permitted dangerous levels of exposure. Since the hazard has been delineated, the standard has been lowered and, as a result, a number of recent studies have developed improved methods for its measurement.

This article reviews the recent literature on measurement of atmospheric vinyl chloride. Measurement methods have been designed primarily to monitor whether or not vinyl chloride concentration is in compliance with the required occupational standards, and to identify unusually high vinyl chloride concentration in a plant for corrective action. The literature which is herein reviewed includes methods for sample collection and analysis and, in addition, describes methods for preparing standard vinyl chloride samples for determining response curves and calibrating measurement procedures.

sampling

grab sampling and liquid scrubbing

Grab sampling and liquid scrubbing are relatively unimportant collection methods for vinyl chloride. Virtually no information was available which evaluated liquid scrubbing.[2] While grab sampling has been used with various evacuated containers, including glass bulbs, stainless steel canisters, gas syringes, and Tedlar bags, it does not appear well suited for occupational sampling.[2,3] Among its disadvantages are its inability to collect a representative sample over a full work shift or large fraction of a shift, cumbersome equipment, and its higher detection limit than collection by adsorption.

adsorption tubes

The most popular measurement method is collection of vinyl chloride by adsorption and

subsequent gas chromatographic analysis. The measurement procedure begins with collection of a field sample by means of a solid sorbent packed into a glass or stainless steel tube. As the atmospheric sample is pumped through the packed tube at a known flow rate and time span, vinyl chloride (as well as other substrates) is adsorbed. The collected sample is then desorbed either by being dissolved in a suitable solvent or by thermal treatment.[2,4,5] Collection by adsorption has several advantages over direct field measurements or grab sampling:

(1) when combined with gas chromatographic measurement, the measurement is the most sensitive;
(2) it is capable of sampling over a larger fraction of a shift;
(3) it is easily applied to occupational compliance measurements and personal sampling;
(4) samples are easily transported and stored.

The National Institute for Occupational Safety and Health (NIOSH) has devised a specific measurement procedure for evaluating compliance. Sampling requires adsorption onto activated charcoal and desorption with carbon disulfide (CS_2).[5-7] NIOSH suggests sampling with commercially available tubes which contain 150 mg of coconut shell charcoal (20/40 mesh) packed into a 4 mm I.D. glass tube. The charcoal is packed into two sections separated by a polyurethane plug: the front section contains 100 mg of charcoal, and the back-up section, which is used to evaluate breakthrough of vinyl chloride from the front section, contains 50 mg of charcoal. If the back section contains more than 20% of the amount found on the front section, the test is not valid. NIOSH[4,5] recommends that 5.0 L of air should be collected at 0.05 L/min with a personal breathing zone sampler, but if high humidity or high concentrations of contaminants are suspected, a 2.5 L sample should be used. However, high humidity or high contaminant concentrations are neither defined nor characterized. After sampling, the tube should be sealed with standard plastic caps. If sample shipment and other factors require more than one day between collection and analysis, NIOSH suggests that the capped tubes should be packed in dry ice for transport and then stored at −20°C until the analysis. Each charcoal section should be analyzed separately. The vinyl chloride is desorbed by adding the charcoal section to a 2 mL vial containing 1.0 mL CS_2 and sealing with a septum cap. The CS_2 samples for GC analysis must be withdrawn by a microliter syringe. NIOSH specifies that the injection should consist of a 5 μL aliquot withdrawn when the charcoal and carbon disulfide have been in contact between 30 and 60 minutes.

Several groups have evaluated the overall NIOSH recommended procedure and its various stages (collection, storage, and desorption). Two studies have evaluated the complete NIOSH recommended procedure.[7,8] Hill, *et al.* reported that the coefficients of variation for samples (5 L) at 7.2 and 71.3 mg/m^3 were 0.076 (27 samples) and 0.075 (29 samples), respectively.[7] They noted that evaluation of the procedure's accuracy is also subject to the experimental errors from preparing the synthetic vinyl chloride atmosphere (*vide infra*). NIOSH estimated the recovery by comparing the concentrations detected by direct GC injection and by the proposed method. For atmospheres containing 2.6 to 64 mg/m^3, the values agreed within ± 6%. Purcell evaluated the method by sampling 1.5 L of an 8 ppm vinyl chloride atmosphere (23 μg vinyl chloride).[8] He reported an analytical recovery of 91.5%, with less than 0.2% on the back section of the sample tube, and a relative standard deviation of 10.6% (for six samples).

Three groups – Hill, *et al.*,[6] Severs and Skory,[9] and Cuddeback, *et al.*[11] – examined breakthrough characteristics in complementary studies. While results generally agreed, the studies did report some conflicting data and conclusions. Cuddeback, *et al.* measured breakthrough with commercial tubes sold by Mine Safety Appliance, Table I.[11] Hill, *et al.* looked at 21 sorbents (of which 6 were activated charcoals and 15 were gas chromatographic packings) packed into 15 mm sections in 4 mm I.D. glass tubes, Table II.[7] Severs and Skory examined several activated charcoals in a series of tests which included packed beds and/or tubes and some commercial tubes.

While Hill and co-workers[7] and Severs and Skory[9] concurred that breakthrough volume

TABLE I
Retention Data for Vinyl Chloride on Charcoal Tubes[A]

Vinyl Chloride Conc. (ppm)	Sample Rate (mL/min)	Mass VCM Flow Rate (μg/min)	Retention Volume (L)[B,C]	Retention Time (min)[B]	Total Mass (μg)[B]
5	50	0 639	10 0	200	127.9
5	100	1 278	9.8	98	125.2
5	150	1.916	29 3	195	373 6
25	50	3 19	7.9	158	504
25	100	6.38	22.8	228	1456
25	150	9 58	20.5	137	1312
50	50	6.38	9.0	180	1285
50	100	12.78	18.1	181	2311
50	150	19.16	14.8	98.7	1891

[A]Standard (150 mg charcoal) tubes from Mine Safety Appliance.

[B]At 10% breakthrough from front section of tube.

[C]Three samples averaged 99 7 mg (±6%) in 16.5 mm (±10.9%) columns.

decreased with increasing flow rate, the data of Cuddeback and co-workers lacked any correlation. Channeling in the commercial tubes was suggested as a possible cause for the inconsistent behavior.[12] If channeling is a real effect in commercial tubes, it is a potential source of error. It would seem, then, that commercial tubes should receive more extensive study.

While most of the data reported by Hill, *et al.*[7] and Severs and Skory[10] agreed, the two groups disagreed on interpretation. Severs and Skory mistakenly challenged the claim of Hill, *et al.* that commercially available (coconut shell

TABLE II
Sorbent Screening Experiments with Vinyl Chloride[7]

	Sorbent	Mesh	Concentration (μg/L)	Sampling Rate (L/min)	Breakthrough Volume[A] (L)
1.	Chromosorb 101-105	60/80	500	1.00	<0.1
2.	Chromosorb 106-107	60/80	500	0.20	<0.1
3.	Tenax GC	35/60	500	0.20	<0.1
4	Silica Gel	20/40	130	0.20	<0.1
5.	Silica Gel w/1% $AgNO_3$	20/40	130	0.20	<0.1
6.	Molecular Sieve, 5A	30/40	500	0.20	2.0[B]
7.	Carbopak A	45/60	500	0.20	<0.1
8.	Carbopak B	45/60	500	0.20	<0.1
9.	Carbosieve B	45/60	500	0.20	2.8
10.	Dow Carbon, XF4175L	20/40	6.5	0.20	5.7[B]
11	Dow Carbon, XF4175L	20/40	6.5	0.15	11.1
12.	Dow Carbon, XF4175L	20/40	6.5	0.10	15.0
13.	Dow Carbon, XF4175L	20/40	6.5	0.05	21.2[B]
14.	Petroleum Charcoal, SKC-104	20/40	6.5	0.10	7.7[C]
15.	Coal Charcoal, BPL	20/40	6.5	0.10	8.2[B]
16.	Coconut Shell Charcoal, MSA-6	20/40	500	1.00	0.9
17.	Coconut Shell Charcoal, MSA-6	20/40	500	0.20	2.4[B]
18.	Coconut Shell Charcoal, MSA-6	20/40	500	0.05	5.2
19.	Coconut Shell Charcoal, MSA-6	20/40	130	0.20	3.4
20.	Coconut Shell Charcoal, MSA-6	20/40	6.5	0.20	5.7
21.	Coconut Shell Charcoal, MSA-6	20/40	6.5	0.10	10.3[D]
22.	Coconut Shell Charcoal, MSA-6	20/40	6.5	0.05	10.7
23.	Coconut Shell Charcoal, SKC-105	20/40	6.5	0.10	10.6[C]
24.	Coconut Shell Charcoal, PCB	20/40	6.5	0.10	8.1[B]

[A]Values are single experiments unless otherwise indicated.

[B]Average of two experiments.

[C]Average of three experiments.

[D]Average of four experiments.

TABLE III
Effect of Charcoal Tube Storage Under Various Conditions on Vinyl Chloride Recovery[11]

Storage Days		High Concentration: 31.9 μg Vinyl Chloride						Low Concentration: 2.6 μg Vinyl Chloride					
		Capped Tubes °C			Fused Tubes °C			Capped Tubes °C			Fused Tubes °C		
		43	22	4	43	22	4	43	22	4	43	22	4
0	Recovery (%)	89	89	89	89	89	89	85	85	85	85	85	85
	Total recovered in back section (%)	0	0	0	0	0	0	0	0	0	0	0	0
7	Recovery (%)	91	71	87	69	79	79	87	84	77	72	86	90
	Total recovered in back section (%)	22	14	3	19	21	3	23	14	0	27	27	10
15	Recovery (%)	78	98	85	60	81	85	76	67	81	64	69	69
	Total recovered in back section (%)	28	20	11	28	23	15	28	18	6	22	19	1

charcoal) tubes could collect 5 L of 206 ppm vinyl chloride at 0.05 L/min without significant breakthrough. They did find breakthrough at 1.5 L for these sampling conditions, but they used commercial tubes containig a petroleum based charcoal (SKC Lot 104) which has a lower adsorption capacity than coconut shell charcoal.[10] A strong point of disagreement between the two groups was the extent that high humidity and/or high concentrations of other contaminants affect breakthrough volume. Both groups agreed that their effect was to reduce breakthrough volume. While Hill and co-workers have suggested that a 2.5 L instead of a 5.0 L sample was sufficient to prevent breakthrough in the recommended commercial 150 mg sampling tube, Severs and Skory have disagreed. They still considered breakthrough a potential problem even with 2.5 L samples and have recommended a commercially available 600 mg charcoal tube for vinyl chloride collection. No information was available to resolve their conflicting conclusions, so this is an important research need.

The effects of storage conditions on the recovery of vinyl chloride collected in commercial tubes were evaluated.[11] The parameters were the tube sealing method (standard caps or fusing the ends), storage temperature (4, 22, and 43°C), storage time (up to 15 days), and the mass of vinyl chloride collected on the front section (2.5 and 31.9 μg). Table III summarizes the results. Among its salient observations, the study demonstrated that the standard caps were sufficient for retaining the vinyl chloride in the tube, and that loss by degradation and/or polymerization appeared negligible. When the tubes were stored for one week at room temperature, a minimum of 14% of the total recovered vinyl chloride migrated to the back section. Cooling the samples to 4°C retarded but did not stop diffusion. Cooling to −20°C seemed sufficient to stop any significant migration. Also, no migration to the back section occurred when 3 μg of vinyl chloride were stored in the front section of a standard charcoal tube at −20°C over a 19-day storage period.[7]

Gas chromatographic packings are capable of adsorbing vinyl chloride.[7,14-18] Hill and co-workers reported that Molecular Sieve 5A and Carbosieve B adsorbs vinyl chloride as well as charcoal, Table II.[7] Bellar,*et al.*[17,18] and Russell[15] also found good adsorption characteristics for Carbosieve B. Bellar and co-workers evaluated adsorbents by collecting vinyl chloride (and other organics) from aqueous samples. Their procedure was to purge a 5.0 mL sample with 150 to 400 mL of nitrogen at 200 mL/min and collect organics on 13 cm columns of test adsorbents. They obtained quantitative recovery of 50 ng of vinyl chloride with silica gel and Carbosieve B. Hill and co-workers, however, have reported that silica gel is a poor adsorbent for vinyl chloride, Table II. The conflicting claims of the two groups cannot be resolved with the evidence at hand. Chromosorbs and Poropaks exhibit good adsorption characteristics for vinyl chloride at ambient temperature.[7,14-18] In addition, Ives has reported good vinyl chloride adsorption on Tenax-GC cooled to dry-ice temperature.[14]

When samples were collected at 0.85 L/min for 35 minutes, recoveries averaged 90% at 6 ppb and 100% at 60 ppb.

Vinyl chloride recovery from the NIOSH recommended CS_2 desorption method ranges from 80 to 90%.[7] Potential sources of loss include gas escape during mixing of CS_2 and charcoal (a highly exothermic process), vinyl chloride partial pressure in the head space of the sample vial, and vinyl chloride adsorption to container and syringe walls. The NIOSH method gave an average recovery of 85% (80 to 90% range) with samples containing 13 μg of vinyl chloride on 100 mg of activated charcoal (charged with 5 L of a 2.6 μg/L vinyl chloride atmosphere). NIOSH also evaluated desorption recovery with 0.5 mL of CS_2 (instead of 1.0 mL), mixing by adding solvent to the charcoal (instead of adding charcoal to CS_2), and mixing at 0°C (instead of mixing at ambient temperature). They found no significant differences for changes in the CS_2 volume or temperature, but found a slightly better recovery when the charcoal was added to the solvent.[7]

Better vinyl chloride recoveries were reported when CS_2 was added to charcoal at temperatures below 0°C.[11,19] Cuddeback, *et al.* desorbed the vinyl chloride by placing the charcoal (100 mg) in a 2 mL glass vial, sealing it with a septum cap, and injecting 0.5 mL of CS_2 while the vial was cooled in dry ice.[11] The vial was then warmed to room temperature and held for 5 minutes before withdrawing samples. Desorption efficiency was 85 and 89% with 2.55 and 31.9 μg vinyl chloride adsorbed, respectively. Lao, *et al.* recommended adding 15 mL of cooled (−15°C) CS_2 to the charcoal (1 g) in a 25 mL reacti-flask fitted with mini-inert valves.[19] The flask was thermostated at +15°C for 15 minutes and then samples were withdrawn for analysis. They reported that head space vinyl chloride concentration never exceeded 2% of the liquid concentration. Recovery ranged from 95 to 97% for 14.1 to 126 ng vinyl chloride and 88% for 2.7 ng vinyl chloride.

Going[13] and Severs and Skory[9] achieved a somewhat greater recovery than the NIOSH workers[4,5,7] by adding charcoal to CS_2 cooled with dry ice. Severs and Skory desorbed 1 g charcoal samples (containing 0.8 μg vinyl chloride) with 10 mL CS_2.[9] Their procedure was to cool the CS_2 (dry-ice temperature), slowly add the carbon to the cold CS_2, agitate the slurry for 30 minutes while cold, and withdraw aliquots for analysis while cooled in a wet ice bath. They achieved a 98% average recovery (range 93-101%). Going also proposed a method in which the charcoal and CS_2 were mixed at dry-ice temperature.[13] The method was to slowly add the charcoal (450 mg) to 2 mL CS_2 in a 3.5 mL vial while it was cooled in dry ice, then seal the vial with a septum cap. Samples (5 μL) were subsequently withdrawn with a microliter syringe while the vial was in dry ice. He recommended a 30-minute contact (recovery was constant from 25 to 140 minutes). For nine samples containing 11 to 13 μg vinyl chloride, recovery averaged 96.6 ± 7.3%. At lower vinyl chloride loadings, the recovery was less (58 to 79% recovery for 154 to 768 ng vinyl chloride).

Other solvents can be used to desorb vinyl chloride from charcoal. An 88% recovery is reported for desorption with tetrahydrofuran; experimental details were not available.[20] Vinyl chloride has been desorbed with a bromine-hexane mixture; in the procedure, vinyl chloride was converted to 1,2-dibromo-1-chloroethane (DB-VC), which has significantly greater sensitivity to electron capture detection (*vide infra*). The procedure consisted of stirring (magnetic stirring bar) 1 g of the activated carbon, 0.5 mL Br_2, and 11 L of hexane in a screwcapped flask at −30°C for 5 minutes. The DB-VC was concentrated by column chromatography on silica gel with hexane followed by evaporation of the solvent. Neither recovery nor precision for the brominehexane desorption was described. DB-VC preparation could be useful as a derivative to confirm apparent vinyl chloride residues.

Thermal desorption has been considered as an alternative to CS_2 desorption for desorbing vinyl chloride from charcoal. Disadvantages of the CS_2 method include the following: CS_2 is very volatile, toxic, and inflammable; vinyl chloride concentration is diluted by a factor of 200; and impurities in the CS_2 can interfere with and/or lengthen analysis time.[8,22] The disadvantage of thermal desorption is that it permits only one analysis per sample, whereas solvent desorption allows multiple analyses.

Three approaches to thermal desorption have been evaluated. Method A desorbed vinyl chloride in an inert gas stream, and all effluent was collected. In Method B, vinyl chloride is eluted onto an analytical GC column and retained through the desorption period. In Method C, the vinyl chloride is eluted into a collection chamber. Then, after the desorption period is completed, the sample is injected onto the analytical column.

Severs and Skory reported the only evaluation of Method A.[9] They recovered 93% of a 25.6 ng vinyl chloride sample by heating the charcoal adsorbent at 430° C in a nitrogen flow of 0.5 to 0.8 L/min. The large effluent volume collected (12 L) is a tedious experimental problem.

The selection of analytical column and analysis conditions are critical for Method B success. Unless the vinyl chloride is retained near the column inlet during the desorption period, peak broadening can occur and reduce sensitivity. Four groups have evaluated this approach.[8,15–18,22] Russell evaluated general methods for analyzing organic vapors, including vinyl chloride.[15] Vapors were collected on various GC packings and were subsequently thermally desorbed. The collection tube was attached to the GC inlet by a Swagelock fitting and wrapped with heating tape. Russell reported only preliminary results for vinyl chloride. It was collected on Carbosieve B and subsequently desorbed (5 minute heating at 270° C) onto a 2 ft. (0.61 m) by 0.125 in. (3 mm) column packed with Carbosieve B. The column was held at 80° C during the desorption period, then programmed to 290° C at 20° C/min. Russell did not report the recovery.

Ahlstrom, *et al.* evaluated vinyl chloride collection and analysis using 150 mg of SKC charcoal (Lot 104), packed into a 5 in. (127 mm) by 3/16 in. (4 mm) U-shaped stainless steel tube.[16] The tube was attached to a GC equipped with a 6 ft. (1.8 m) by 1/8 in. (3 mm) stainless steel column packed with Poropak QS (80/100 mesh). The oven temperature was 90° C, and the carrier gas (nitrogen) was maintained at a flow rate of 0.20 L/min. Vinyl chloride was desorbed by heating the U-tube at 400° C (pulse heater) for two minutes. They reported apparent recovery of 96 to 102% for 5.8 to 17.3 μg vinyl chloride added to the charcoal. Relative standard deviation of four samples charged with 1 ppm vinyl chloride was 1.2%. The average retention time for vinyl chloride was 6.50 min.

Purcell and Giordano[8,22] desorbed vinyl chloride from commercial activated charcoal tubes. They transferred the charcoal containing the vinyl chloride from the sampling tube to a standard glass liner built for the Perkin-Elmer Series 900 GC system.[8,22] The analytical column was a 1.5 ft. (1.6 m) by 1/8 in. (3 mm) stainless steel column packed with Chromosorb 102 (80/100 mesh). The conditions were a 70° C oven temperature and carrier gas flow (helium) at 0.040 L/min. They desorbed vinyl chloride by heating the charcoal at 260-300° C for four minutes. During the desorption period, the column was held at ambient temperature (by keeping the oven door open). At the end of the heating period, the oven door was closed and the column was rapidly heated to the operating temperature (70° C). Purcell and Giordano reported recovery of 90 ± 4.1% for 717 ng of vinyl chloride. Retention time for vinyl chloride was 3.2 minutes.

Bellar and co-workers developed an apparatus and a procedure for desorption of organics collected on silica gel and Carbosieve-B (*vide supra*).[17,18] They designed two desorber units. Desorber No. 1 works with the trap fit within the gas chromatograph injection port and is heated by the injection port heating block. They designed Desorber No. 2 for gas chromatography units where Desorber No. 1 will not fit into the injection port. Desorber No. 2, which is equipped to heat the trap by means of a heater wire insulated with asbestos, is attached to the gas chromatograph by a needle through the injection septum. Both Desorbers No. 1 and 2 are equipped with a backflush flow controller which purges the trap with a gas source (other than the GC carrier gas). The analytical column was a 6 ft. (1.8 m) by 1/8 in. (3 mm) stainless steel column packed with Chromosorb 101 (60/80 mesh) at 90° C or programmed from 90 to 200° C at 10° C/min, and the carrier gas was nitrogen at a flow rate of 0.060 L/min. They held the GC at ambient temperature during the desorption period (oven door left open). During desorption, the trap was heated to 150° C with 0.020 L/min nitrogen flow for four minutes. Then the backflush flow controller was removed and the GC temperature program was initiated. Bellar

and Lichtenberg reported quantitative recovery of 50 ng of vinyl chloride from either Carbosieve B or silica gel.[18]

Vinyl chloride desorption by Method C has been evaluated in two studies – Meyers, *et al.*,[23] and Ives.[14] Meyers and co-workers prepared sample tubes by packing activated charcoal (60/80 mesh) in columns 6.5 cm long inside 5 mm O.D. glass tubing. The tubes, which were exposed to 1 L of 1 ppm vinyl chloride, were heated at 300°C for 30 seconds in a Burrell Pyrolizer. Then the desorbed vinyl chloride was passed through a 1/8 in. (3 mm) stainless steel tube and onto the analytical column 6 ft. (1.8 m) by 1/8 in. (3 mm) Chromosorb 101, which was operated at 100°C. They reported an average vinyl chloride concentration of 1.25 ± .037 ppm for 13 replicate samples. They found that 20 ppb could easily be detected with a 5 L sample and suggested that as low as 1 ppb could be detected by increasing the attenuation of the GC. Ives studied collection and desorption with Tenax-GC.[14] The tube, which was wrapped with heating tape, was heated at 150-180°C for five minutes. Then desorbed vinyl chloride was injected onto the GC through a Hamilton syringe valve in the injection port. The GC column was a 6 ft. (1.8 mm) by 4 mm glass tube packed with Poropak QS and heated at 120°C. The system was tested with 6.5 cm columns of Tenax-GC packed into 5 mm I.D. glass tubes and exposed to 2.975 L of a standard vinyl chloride atmosphere. With 60 ppb vinyl chloride, the recovery was 100% (three samples), and for 6 ppb it averaged 89.6 ± 4.7% (thirteen samples).

automated sample collection

An automated sampling system was developed for monitoring an industrial plant.[24] Each sampling station collects atmospheric samples through a cartridge filter which is protected from rain by an inverted 6 in. (15 cm) funnel. The sample flows from the sampling station to the laboratory through 1/4 in. (6 mm) stainless steel tubing. Samples are analyzed by means of gas chromatography (0.5 mL injections) and require 2 minutes for the complete analysis. The system can collect and analyze 20 samples per hour – 19 plant sites and 1 calibration sample (10 ppm vinyl chloride in nitrogen). Baker and Reiter claimed reproducibility within ± 0.1 ppm for a 1 ppm sample when the system was set to measure the range 0-25 ppm.

analysis

gas chromatography

Gas chromatography is the most sensitive, accurate, and dependable method now available for vinyl chloride analysis. Salient features in the GC procedure are the analytical column, detector to remove potential interferences (substrates detected along with the vinyl chloride), and procedures to optimize the rapidity and cost for an analysis. Optimal cost and speed of analysis depend upon methods to remove interferences, vinyl chloride retention time, and either backflushing or increasing oven temperature to remove substrates of high retention time from the analytical column.[8,24] The important considerations in the choice of a detector include detection limits, linearity of response, specificity, and expense. Table IV compares the specificity and lower limits for several detectors.

The flame ionization detector (FID) which is recommended by NIOSH[4-7] is an excellent general purpose detector. Its advantages include a low vinyl chloride detection limit (100 pg), a good linear response range, and inexpensive operation. Its major disadvantage is its nonselective response.

Microcoulometry can be operated specifically for organohalides. The method requires substrate pyrolysis, then assays of the released halide ion. The Hall detector is reportedly the most sensitive of the available microcoulometric detectors for chloride. Its reported detection limit for vinyl chloride of 0.07 ng is slightly better than the FID detection limit.[26,27] Its major advantage is its sensitivity to organohalides. Since the detector is virtually blind to non-halogenated substrates, it eliminates interferences from potentially troublesome, low molecular weight hydrocarbons and other organics, such as acetaldehyde (see Table IV).

Although mass spectrometry - specific ion monitoring (SIM) offers excellent selectivity and the lowest detection limit (20 pg), its expense places it out of reach of most laboratories. Vinyl chloride is monitored by its parent ions, m/e 62 (^{35}Cl) and 64 (^{37}Cl). The individual ions are not

TABLE IV
Comparison of Gas Chromatography Detectors for Vinyl Chloride Analysis[2,3,25-29]

Detector	Specificity	Approximate Detection Limit (g)
Flame ionization detector	none	0.1×10^{-9}
Electron capture	halides	2.0×10^{-9}
Microcoulometry (Hall detector)	halides	70×10^{-12}
Chemiluminescence	olefins	20×10^{-9}
Mass spectroscopy - specific ion monitoring	m/e 62 and 64 ions	$10\text{-}20 \times 10^{-12}$

always specific for vinyl chloride.[19,25] For example, SO_2^+ appears at m/e 62, and CF_2^+ appears at m/e 64. Since the natural isotope distribution of ^{35}Cl to ^{37}Cl is 3:1, vinyl chloride can be specifically monitored by measuring the parent ion isotopic ratio.

Electron capture detection (ECD) is not as selective as microcoulometry, but is more selective than FID. Its major disadvantages are that the response for vinyl chloride is low relative to aromatic halides and to multiple chlorinated hydrocarbons (for example, trichloroethylene has a sensitivity of 0.020 ng compared to 2.3 ng for vinyl chloride), temperamental operation, and a relatively small dynamic response range.[2] The ECD limit for vinyl chloride was reduced by brominating vinyl chloride to yield 1,2-dibromo-1-chloroethane (DB-VC) (*vida supra*). The detection limit for DB-VC was 15 pg and the response curve was linear in the range of 50-300 pg.

The chemiluminescence detector, which is specific for olefins, is a relatively recent system based upon the chemiluminescence of the excited reaction products of olefins and ozone.[23,28,29] McClenny and co-workers compared the detector response for vinyl chloride with several low molecular weight olefins (ethylene, propene, butene, butadiene, and 1,2-dichloroethylene) and found that it yielded the poorest response.[28] Its detection limit was about 20 ng.

A number of GC analytical columns have been found adequate for the separation; Table V summarizes some of the packings and operating temperature ranges for vinyl chloride analysis. Most of the columns and conditions yield vinyl chloride retention times of less than five minutes.

Baker and Reiter utilized three columns for analysis. The first two columns consisted of 20% Igepal CO-880 on Chromosorb P and the third column was 20% Octoil S on Chromosorb P.[24] After higher boiling components of a sample were removed on the first column, the second column separated vinyl chloride from most of the remaining interfering components. The final separation was achieved on the third column.

A major analytical problem is to insure that other substances do not interfere with vinyl chloride measurement. Potential interferences include light hydrocarbons, Freon 11 and 12, acetaldehyde, and SO_2.[9,13,14,25,26,31] Specific interferences vary between columns. Table VI summarizes relative retention time data for potential interferences with Chromosorb 102, Poropak Q, and Carbowax 1500 on Carbopak A.

Acetaldehyde is probably the most common interference for vinyl chloride. A specific method was developed to quantitatively remove acetaldehyde interference from the vinyl chloride analysis.[30] The method uses a 6 in. (15 cm) by 1/8 in. (3 mm) stainless steel column packed with a mixture of sodium bisulfite and glass wool ahead of a 6 ft. (1.8 m) by 1/8 in. (3 mm) Poropak Q column. The acetaldehyde forms a bisulfite complex on the precolumn.

other analytical methods

Infrared analysis has been used to monitor vinyl chloride concentration directly in the field. Portable meters equipped with 20.25 m folded-path absorption cells yield a detection limit of about 1 ppm at the 941 or 917 cm^{-1} bands.[2,35,36] However, many other substances can interfere with the analysis. The potential interferences

TABLE V
Common Packings and Oven Temperatures for the Vinyl Chloride Analysis

Column Packing	Oven Temperature (°C)	Reference
10-20' (3-6 m) SE-30 on Chromosorb G, Chromosorb W, or Anakrom ABS	Ambient to 90	7,25,26
20' (6 m) 10% FFAP on Chromosorb W	65	7
6' (1.8 m) Poropak Q	100-135	11,30,32
5-6' (1.5-1.8 m) Poropak QS	70-120	9,14,16
6' (1 8 m) Chromosorb 101	90-100	18,23
1 5-6' (0.5-1 8 m) Chromosorb 102	70-145	8,13,19,33
6' (1.8 m) 10-20% DC 200 on Chromosorb W or Supelcoport	80	9,13
20' (6 m) Carbowax 4000 on Supelcoport	80	9
6' (1.8 m) 0 4% Carbowax 1500 on Carbopak A	Ambient	13,28
6' (1 8 m) 5% OV-101 on Chromosorb W	Ambient	32
6' (1 8 m) 10% Apiezon M on Chromosorb W	Ambient	32
6' (1.8 m) Silica gel	30	34
300' (90 m) Open tubular column, coated with dibutyl maleate	0	34
16' (4 8 m) 16 7% triscyano ethoxy-propane on Chromosorb W	Programed from 50 to 170	31

include allyl chloride, ethylene, Freon 12, methacrylonitrile, perchloroethylene, styrene, tetrahydrofuran, trichloroethylene, and vinylidene chloride.[2] While infrared analysis appears useful for surveys to monitor vinyl chloride spills in high-risk areas, it does not appear to be sufficiently sensitive or specific for routine monitoring.

A continuous system for vinyl chloride monitoring using conductivity measurement has been developed.[37] As the air is sampled, the vinyl chloride is continually degraded as the airstream is passed through a 6 in. UV lamp operated at 253.7 nm. The degradation efficiency for this procedure was 80%. Vinyl chloride concentration was then measured by conductivity with a Davis Instrument Series 11-7000 Sulfur Dioxide Meter. With a 2.5 minute hold-up time in the Davis Meter, response reached 90% of the final reading. Confer found a lower detection limit of 0.05 ppm and a linear response up to 25 ppm.[37] The method does have several potential interferences. Some interferences can be removed by passing the airstream through a water scrubber prior to the degradation; these removable interferences include sulfur dioxide, carbonyl sulfide, hydrogen sulfide, and chlorine. Interferences which are not removed by the water scrubber include nitric oxide, carbon disulfide, methyl chloride, and trichloroethylene.

Preliminary results of Stark spectroscopy for field measurement of vinyl chloride were reported.[38] The system used either a carbon dioxide or carbon monoxide laser with an absorption cell consisting of two 40 cm stainless steel Stark electrodes spaced 1 mm apart. The method, which is capable of measuring vinyl chloride at the ppm level, is currently in the experimental stage.

vinyl chloride standard samples

Standard samples are required for calibration purposes in vinyl chloride collection and analysis. The most important standard samples are for use in the NIOSH recommended method

TABLE VI
Relative Retention Times of Potential Interferences to Vinyl Chloride
(Relative Retention = 1.0)

Compound	Chromosorb[A] 102	Chromosorb[B] 102	Poropak Q[C]	0.4% Carbowax[D] 1500 on Carbopak A
Methane	0 15	--	0.05	0 20
Ethane	0 21	--	--	0 29
Ethene	0.21	0.33	--	0.26
1,1-Difluoroethylene	--	0.33	--	0 63
Propene	--	0.62	0.46	0 63
Propane	0 54	--	0.52	0.63
Methylacetylene	--	--	0.56	--
Methyl chloride	0.63	--	0.57	0.45
1,1-Difluoroethane	--	0.51	--	--
Chlorodifluoromethane	--	0.53	--	--
Cyclopropane	--	--	0.59	--
Formaldehyde	--	--	0.62	--
1-Chloro-1,1-difluoroethane	--	0.92	--	--
Acetaldehyde	0.93	--	0 95	0 77
Freon 114	--	1 21	--	--
Isobutane	1.22	--	--	--
Isobutylene	1 37	1.25	--	--
Methanol	--	--	--	1.38
1,3-Butadiene	1.57	1.27	--	--
1-Butene	1 43	1 30	--	--
Vinyl methyl ether	--	1.36	--	--
Trans-2-butene	1.57	1.38	--	2.92
Ethyl chloride	1 70	--	--	1.54
Cis-2-butene	1.73	1.43	--	--
Vinyl bromide	--	1.85	--	--
1,1-dichloroethylene	2.00	--	--	--

[A] 6' × 1/8" Chromosorb 102 (80/100 mesh) at 100°C[13]
[B] 6' × 1/8" Chromosorb 102 (80/100 mesh) at 145°C[19]
[C] 6' × 1/8" Poropak Q (80/100 mesh) at 100°C[12]
[D] 6' × 1/8" 0 4% Carbowax 1500 on Carbopak A at ambient temperature[13]

of collection on activated charcoal and GC analysis.[4,5] The NIOSH recommended procedure uses standard atmospheres for determining analytical recovery and standard solutions (in CS_2) for preparing GC response curves. Since vinyl chloride is a gas at ambient temperature, the standard samples are prepared by volumetric and gravimetric methods which are common in gas handling.[2-5,7,9] Standard atmospheres have been prepared by diluting a known volume of vinyl chloride with an inert gas in a gas bag made of material such as Tedlar.[3,4] Standard solutions have been prepared by volumetric and gravimetric methods. NIOSH suggested either adding known volumes of vinyl chloride by gas syringe to the solvent or adding vinyl chloride to toluene, measuring the weight gain, and then diluting the sample with CS_2 (the solvent) to the final concentration.[3,4] Severs and Skory sealed a known weight of vinyl chloride in an all-glass ampul and then broke the ampul in the solvent.[9]

The permeation tube for generating synthetic vinyl chloride atmospheres is an excellent alternative.[39-41] While precision for preparing a 1 ppm vinyl chloride atmosphere by the gas dilution method is about 10%, the permeation tubes yield a 1 ppm atmosphere with a standard deviation of 2%.[40] The permeation tube consists of a plastic-walled tube filled with vinyl chloride and plugged at both ends. The vinyl chloride diffuses through the plastic walls of the tube (Fick's Law of Diffusion) at a rate which is constant and also temperature dependent (a temperature variation of 0.1°C will create a 1% error in vinyl chloride concentration). FEP (fluorinated ethylene copolymer) tubes have generally been chosen;[39-41] vinyl chloride diffusion remains constant for at least eight months with FEP tubes.

The vinyl chloride permeation rate can be determined either by measuring the weight of vinyl chloride lost from the tube or the vinyl chloride released with time. To measure

diffusion rate by weight loss from the tube, about three weeks are required to create sufficient accuracy. Cedergren and Fredrickson have developed a rapid (about one hour), accurate method for measuring the released vinyl chloride.[39] The diffused vinyl chloride is combusted at high temperature to yield hydrogen chloride (HCl), which is assayed by coulometric titration with silver in 70% acetic acid. They compared the gravimetric and coulometric methods for the permeation rate measurement.[39] While the gravimetric method yielded a mean vinyl chloride diffusion rate of 0.464 ± .002 μg/hour, the coulometric method value was 0.463 ± .001 μg/hour.

Synthetic vinyl chloride atmospheres are generated by placing the permeation tube in a thermostated chamber which contains two openings. The dilutent gas is metered into the chamber in one opening and the standard atmosphere is sampled through the second. Cedergren and Fredrickson prepared a 1.000 ± .002 ppm vinyl chloride atmosphere (calibrated by coulometric titration).[39]

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Sorry, wrong number . . .

The telephone number supplied as a contact for further information in the announcement "HEW 1979-1980 Fellows Program announced . . .", *Am. Ind. Hyg. Assoc. J. 39*:997 (December, 1978), is incorrect. Calling the number published will put you in contact with an irate gentleman in New Jersey, rather than HEW. The correct number to call is (202) 245-6087. Our apologies for any inconvenience this combination of typesetting and proofing errors may have caused you.

Sorry, no number . . .

The editorial feature "New digest charts OSHA toxic substance regulations", published in October, 1978 (*Am. Ind. Hyg. Assoc. J. 39(10)*:A-26,27) has generated a gratifying amount of interest. An address was shown in the body of the information on which the article was based, but no phone number was included. Since the address was a P.O. Box number, those trying to obtain a number to make inquiry by telephone could not do so. The Postal Service will not release any identifying information regarding box holders. Investigation by the JOURNAL reveals that the individual to contact is Harry B. Burr. He can be reached by phone at (412) 255-3476. It is suggested that this information be noted in your October issue, for possible future use.