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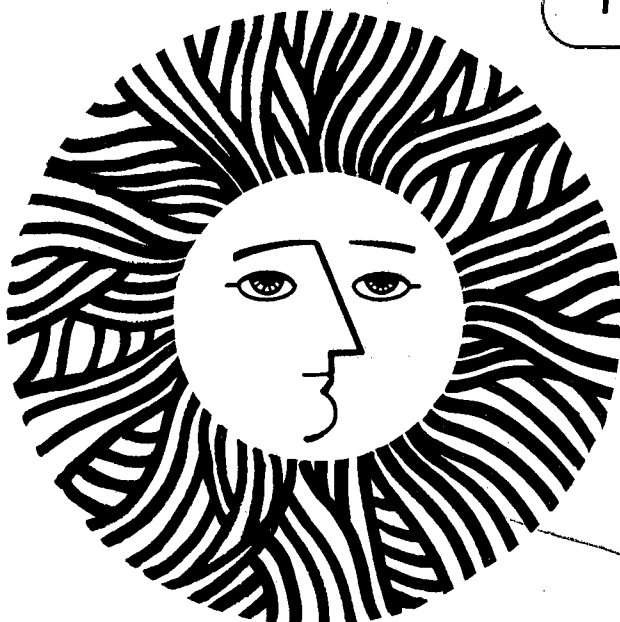ANALYTICAL METHODS FOR THE DETERMINATION OF ALDEHYDES

R.R. Miksch, D.W. Anthon, L. Zebre
and C.D. Hollowell

September 1981

## DISCLAIMER

ANALYTICAL METHODS FOR THE DETERMINATION OF ALDEHYDES

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## ABSTRACT

A review of analytical methods for the determination of aldehydes with 140 references. Excerpted from material presented in <u>Formaldehyde and Other Aldehydes</u>, National Research Council, National Academy of Sciences, National Academy Press, Washington, D.C., 1981.

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# ANALYTICAL METHODS FOR THE DETERMINATION OF ALDEHYDES

## INTRODUCTION

Air-quality standards and pollution-control legislation are generally based on the assumption that exceeding a threshold concentration of any given pollutant will have harmful effects on human health. Accurate determination of such "threshold concentrations" demands accurate methods of analysis.

This report discusses analytical methods currently used for aldehydes, including techniques of sampling and calibration, and other available or potentially available methods. In general, the analytical methods for aldehydes are difficult, and much developmental work is needed. Where possible, estimates of the accuracy, precision, and applicability of the various measurement methods are presented.

## METHODS OF GENERATING STANDARDS

All methods of analysis have in common the need for calibration. Calibration is performed by applying the chosen method of analysis to a standard. The standard can be prepared by weighing (a primary standard) or measured by an independent primary reference method of analysis (a secondary standard). In the case of aldehydes, the standard is usually a liquid solution or a gas-phase mixture of one or more aldehydes. Liquid solutions are static; gas-phase mixtures can be static or dynamic (i.e., generated continuously). This section discusses the preparation of standards and their application to calibration.

### STATIC METHODS

Aqueous solutions of aldehydes can be used as standards for calibration. The solutions are usually obtained by dissolving an appropriate amount of the desired aldehyde in water. Ordinary reagent-grade aldehydes are often used without purification, although for accurate work it is imperative to distill the aldehyde before use, because oxidation and polymerization occur on standing.

Primary standardization can be achieved by straightforward application of gravimetric or volumetric methods. It is also possible to prepare a secondary-standard solution of aldehyde by oxidative titration. Two methods described by Walker[133] are suited to the analysis of aldehydes other than formaldehyde: the alkaline peroxide and iodometric methods, which rely on the oxidation of an aldehyde to its corresponding carboxylic acid. Once oxidized, the acidic solution can be titrated. These reactions are characteristics of all aldehydes, so there should be no problems in applying the methods to the preparation of a secondary-standard solution of any (pure) aldehyde.

It is difficult to prepare a primary-standard solution of formaldehyde, because pure formaldehyde is not readily available. There are, however, two ways to prepare formaldehyde solutions for standardization

by a primary reference method. The easier (but less desirable) is to dilute commercial formalin (37% formaldehyde w/w) to the approximate desired concentration. Unfortunately, solutions so obtained will contain methanol, which is added to formalin as a stabilizer, as an impurity. A methanol-free formaldehyde solution can be obtained by refluxing an appropriate amount of pure paraformaldehyde in water and filtering the resulting solution.

For standardizing formaldehyde solutions prepared by these methods, Walker[133] described several methods. A simple and accurate primary reference method involves the addition of an aliquot of formaldehyde solution to a neutral solution of sodium sulfite to form a bisulfite addition product and sodium hydroxide. The hydroxide released can be neutralized with a primary acid standard to standardize the solution. The neutralization can be monitored with a pH meter.

A second method is the bisulfite-iodine titration procedure.[9, 130] Excess sodium bisulfite is added to the formaldehyde solution to form a bisulfite-formaldehyde adduct at neutral pH. The unreacted bisulfite is then destroyed with iodine. Addition of a carbonate buffer releases the bisulfite from the bisulfite-formaldehyde adduct, and the freed bisulfite is titrated with iodine (starch is used on an indicator). The iodine solution itself must be standardized with sodium thiosulfate. The method is complex and has several sources of possible error.

Standardization methods based on bisulfite are recommended for use only with formaldehyde, because the formation of the bisulfite-aldehyde adduct with other aldehydes may be less than quantitative.[133]

## DYNAMIC METHODS

Aldehydes are reactive compounds, so it is difficult to make calibration gases that are stable for a useful period. This precludes the use of gas-tank standards, unless the concentration of aldehyde is very high (several percent). Recent advances in rendering gas-tank surfaces inert may alter this situation, but no data are available. For most applications, it is currently necessary to use dynamic methods to generate gas-phase aldehyde standards.

Permeation tubes have been used to generate dynamic gas standards for many different types of compounds and can be used for aldehydes as well. These tubes contain pure compound in a length of Teflon tubing capped at both ends. Over time, material diffuses through the Teflon wall at a low and constant rate, provided that the temperature is held constant.[113] Tubes for acetaldehyde, propionaldehyde, and benzaldehyde are commercially available, and tubes could undoubtedly be constructed for other aldehydes. These tubes are calibrated gravimetrically (and are thus classified as primary reference standards) and can be used with a constant-flow system to generate primary gas standards in the concentration range of parts per billion to parts per million.

Permeation tubes containing pure formaldehyde do not exist. The vapor pressure of pure formaldehyde would be too high to permit the construction of permeation tubes, if it were not already prone to

polymerization at room temperature. Construction of a permeation tube for formaldehyde has been attempted with paraformaldehyde. At 80° C, the decomposition rate of the polymer is great enough that a usable permeation rate can be obtained. However, the gas in equilibrium with paraformaldehyde is not pure formaldehyde; it contains substantial amounts of methylal, methyl formate, orthoformate, and water.[133] Thus, co-emission of these gases with formaldehyde from the paraformaldehyde permeation tube may make gravimetric calibration impossible.

One of the simplest methods for generating a gaseous aldehyde is to use the headspace vapor of an aqueous solution of the aldehyde. This method has been used to generate acrolein for use in assessing molecular sieves as aldehyde adsorbents.[45] The method is especially applicable to the generation of gaseous formaldehyde standards. It must be noted that, because formaldehyde is almost entirely hydrated to methylene glycol, $CH_2(OH)_2$, in aqueous solution, it has a much lower vapor pressure than would otherwise be expected. The apparent Henry's law constant (2.77 torr/mol-fraction) for formaldehyde was determined in 1925 by Ledbury and Blair.[72]

Use of aqueous headspace vapor does not provide a primary standard directly. The gas must be standardized in a secondary manner--usually by measuring the amount of aldehyde lost from the solution. It is possible to assess the efficiency of a collection device by comparing the amount lost from a source solution with the amount of aldehyde trapped.

A second, related method for generating gas-phase aldehyde standards involves the slow addition of a dilute aqueous solution of an aldehyde to a gas stream in such a way that the aldehyde solution evaporates entirely. By knowing the rate at which the aldehyde is being added to the gas stream and the flow rate of the dilution gas, one can determine the aldehyde concentration in the gas stream. A device implementing this method was constructed with a syringe pump to inject the aldehyde solutions into a heated section of tubing through which the dilution gas was flowing.[73, 137] The purity of the gas standards generated by this method depends on the purity of the liquid solutions. In the case of formaldehyde, again, it is desirable to use methanol-free formaldehyde solutions. Gases made this way will contain a great deal of water (as occurs with the headspace technique), which is undesirable in some cases. There may also be some decomposition of aldehyde.[73] As a secondary reference method, the technique must be used with caution.

A promising, although relatively unused, technique that has been used to generate low concentrations of aldehydes involves the thermal or catalytic decomposition of precursor compounds. In one study, formaldehyde was generated through the decomposition of a gas stream of S-trioxane (the cyclic trimer of formaldehyde) as it passed over a phosphoric acid-coated substrate.[44] In a second study, olefinic alcohols were thermally decomposed into a mixture of an aldehyde and an olefin (e.g., 3-methyl-3-butene-1-ol gives formaldehyde, 4-pentene-2-ol gives acetaldehyde, and 5-methyl-1,5-hexadiene-3-ol gives acrolein). The olefinic alcohol was introduced into the gas phase with a diffusion or permeation tube and then decomposed in a heated gold tube. Decomposition of the parent olefinic alcohol is virtually quantitative, so the

technique generates a primary standard. It is also possible to use gas chromatography as a secondary reference method to analyze for the olefin produced in the reaction. When this method is used to generate standards for gas-chromatographic analytic techniques, the olefin can be used as an internal standard. One advantage of this method is that undesirable compounds are never handled in bulk, inasmuch as they are generated only in small amounts as they are used. This method has been used to generate standards of formaldehyde, acetaldehyde, and acrolein as low as a few parts per million.[127] Other thermal decompositions of precursor compounds have been used to obtain vinyl chloride and acrylonitrile.[39]

## AIR SAMPLING

An essential aspect of any analytic technique is the method of sampling. Choice of a method of sampling must be consistent with the information desired. Techniques that take an integrated sample over a long period can concentrate pollutants and simplify analysis. Such techniques are applicable when the determination of mean exposure is desired. Techniques that provide real-time measurements usually require sophisticated equipment, but may be required when it is desirable to observe concentration fluctuation during a short period. In the monitoring of compliance of pollutant concentrations with specific values set by a government agency, high precision is needed; in the study of trends, it is more important to have a reproducible method.

In the analysis of air pollutants, both direct and indirect sampling methods may be used. The direct method uses such instruments as infrared and microwave spectrophotometers, which are capable of measuring the concentrations of compounds in situ. Direct sampling techniques and direct investigative methods are discussed later in this chapter. When the compounds of interest are present in extremely low concentrations, thus precluding direct measurement, or when sampling sites are inaccessible to sophisticated instruments, indirect sampling techniques are commonly used.

Indirect sampling can consist merely of taking a representative grab sample. Air to be sampled is admitted into a previously evacuated vessel or pumped into a deflated bag. Inert materials--such as Teflon, Tedlar, and stainless steel--are used to construct grab-sampling containers. The sample is returned to a central laboratory and analyzed as though the measurement were being made in situ.

Grab sampling suffers from two defects. Because no preconcentration has been effected, the laboratory measurement technique must be sensitive enough to determine ambient concentrations directly. A more serious problem arises from the relatively long time that the low concentrations of the pollutants to be measured are in contact with the high surface area of the grab-sampling container. Nonspecific adsorption can occur, and a substantial fraction of the sample may be lost. The container may develop a "memory" and give rise to spuriously high determinations on successive samples. Careful calibration and scrupulous analytic technique may minimize this latter defect.[28, 94, 116, 137]

## PRECONCENTRATION SAMPLING WITH SUBSEQUENT ANALYSIS

A common indirect sampling technique involves preconcentrating the sample at the sampling site, e.g., by passing air through an absorbing liquid. There are two advantages. Preconcentration makes analysis in a laboratory easier, inasmuch as a higher detection limit can be tolerated. And preconcentration often stabilizes the sample. In sampling for aldehydes, preconcentration techniques are almost always used.

As noted previously, preconcentration devices are generally used in sampling aldehydes in ambient air. Impingers are used most often for trapping low-molecular-weight aldehydes. Many types of impingers have been constructed to accommodate different sampling applications (Figure 1).

If the collection efficiency of the trapping solution is less than 100%, it is desirable to use more than one impinger in series. A typical arrangement for the sampling of formaldehyde (as recommended by NIOSH[130]) consists of two midget impingers in series, each containing 10 ml of water. The sample is collected at a flow rate of 1 standard liter per minute (slpm). The final solution is analyzed colorimetrically.

It is desirable to use an ice bath or a refrigerated sampler with impingers. Otherwise, low relative humidity or high ambient temperature may cause the impinger solution to evaporate, thus limiting the sampling time. The solubility and stability of the aldehyde in the trapping solution may also be adversely affected if impingers are not kept cold.

Figure 2 shows two designs for aldehyde samplers used by Miksch et al.[86] The impinger sampling trains are contained in a small refrigerator. One sampler has a separate flow-control system that can sample air at a constant mass flow rate even when the pressure drop across the sampling train varies. The second sampler uses a critical orifice for flow control.

The absorbing solution used in the impinger depends on the aldehyde to be analyzed. In many cases, the solution contains a trapping reagent that is a constituent of the analytical procedure, thus simplifying operations. In general, there are two categories of trapping solutions for aldehydes. The first "category" is simply water. Formaldehyde reacts rapidly with water to form the relatively nonvolatile hydrate, methylene glycol. Methylene glycol does have a finite vapor pressure, however, and saturation may occur if sampling times are excessively long. This problem can be minimized by using two impingers in series. The collection efficiency of a single impinger containing water will decrease with time, but two impingers in series will maintain a collection efficiency of over than 95% for sampling times of over 48H.[86]

Water does not appear to be an especially good reagent for trapping higher-molecular-weight aldehydes, because the equilibria do not favor the formation of the hydrates.[15] To use aqueous bubblers to trap higher-molecular-weight aldehydes, an additional carbonyl scavenger must be present in the trapping solution. Carbonyl scavenger compounds constitute the second category of aldehyde-trapping solutions.
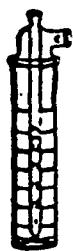
a. Midget Impinger.
   Ace Glass Co.

b. Midget Gas Bubbler (coarse frit).
   Ace Glass Co.
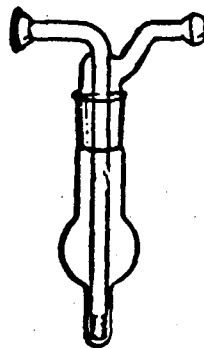
c. Nitrogen Dioxide Gas Bubbler.
   Ace Glass Co.
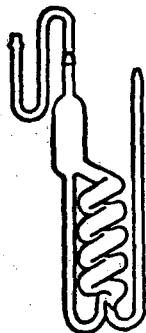
d. Spiral Type Absorber.
   American Society for Testing Materials:
   Tentative Methods of Sampling Atmos-
   pheres for Analysis of Gases and Vapors,
   Philadelphia, PA, July 24, 1956.
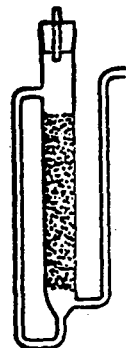
e. Packed Glass-Bead Column.
   American Society for Testing Materials:
   Tentative Methods of Sampling Atmos-
   pheres for Analysis of Gases and Vapors,
   Philadelphia, PA, July 24, 1956.
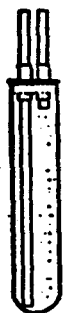
f. Midget Impinger.
   Lawrence Berkeley Laboratory.

g. Bubbler Absorber with Diffuser.
   American Society for Testing Materials:
   Tentative Methods of Sampling Atmos-
   pheres for Analysis of Gases and Vapors,
   Philadelphia, PA, July 24, 1956.

FIGURE 1   Various types of impingers used to sample air. a-e and g reprinted
with permission from Pagnotto;[98] f from R.R. Miksch unpublished observations.

## Sampler With Separate Flow Control
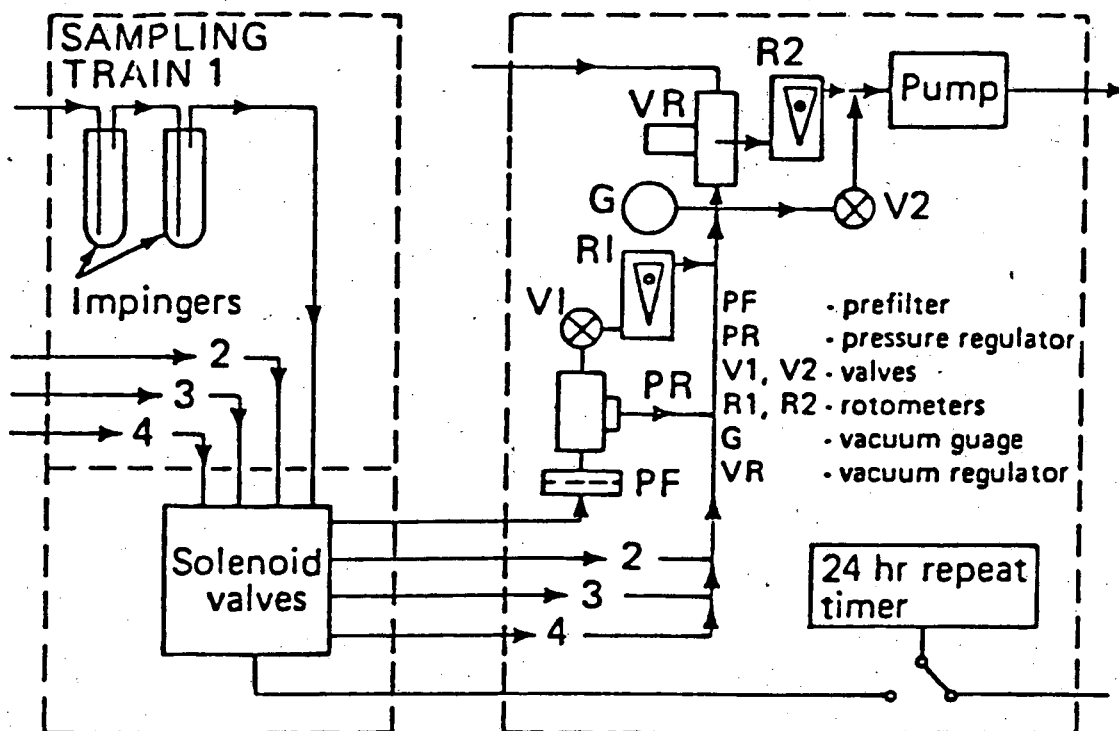


## Sampler With Self - Contained Flow Control
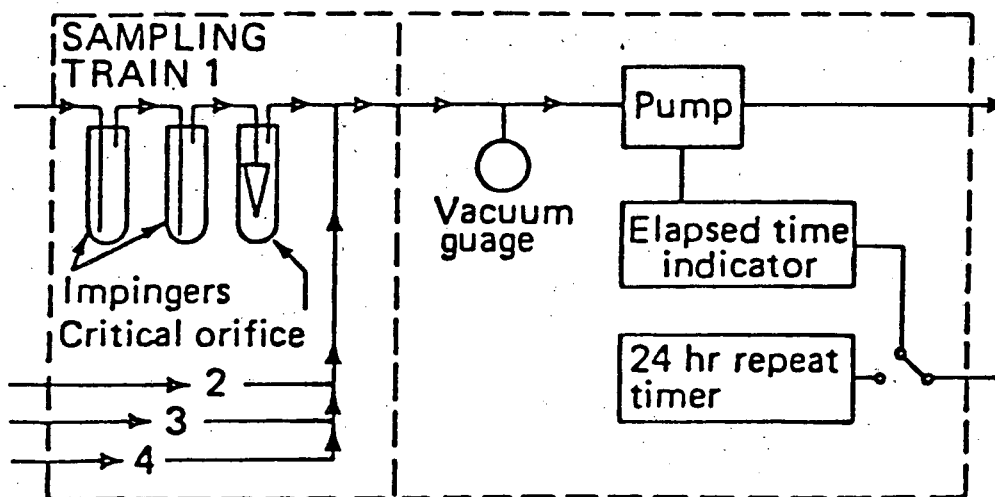


FIGURE 2   Sampling systems for sequential sampling of formaldehyde/aldehydes. Reprinted with permission from R.R. Miksch.

The scavengers are chosen for their ability to react rapidly and quantitatively with carbonyl-containing compounds to form nonvolatile adducts. The reagents selected have included bisulfite, hydroxylamine, semicarbazone, and several phenylhydrazines, all of which have been shown to react extremely rapidly with aldehydes.[16] Table 1 shows the collection efficiency for different aldehydes of various trapping solutions that contain scavengers. The data are compiled from a number of sources and are not always consistent, owing to the different experimental conditions used. The choice of a carbonyl-scavenger trapping agent depends on the analytical method to be used.

Higher-molecular-weight aldehydes also have been detected by means of solid adsorbents. The most widely used solid adsorbent is the porous polymer Tenax-GC, which has been used extensively to measure atmospheric organic compounds, including aldehydes, at low concentrations. In practice, the procedure is best suited for organics in the range $C_6$ to $C_{12}$. Pellizzari[99, 100] has reported finding several aldehydes in ambient air with this method.

Other solid adsorbents also have been used. Molecular sieves have been used to capture low-molecular-weight aldehydes by physical entrapment. Samples can be desorbed with water for analysis by gas-chromatographic or colorimetric techniques. Formaldehyde, acetaldehyde, and acrolein have all been detected with molecular sieves, but quantitation data are available only on acrolein.[45] The solid absorbents charcoal and silica gel have also been investigated, but the results have not been promising. It has been difficult to effect quantitative desorption of collected aldehydes.

It should be noted that a standard source of aldehyde gas is not required to estimate the collection efficiency of a given sampling device. Several devices can be placed in series and the fraction of the total sample collected in each device determined. This technique has been used to obtain collection efficiencies,[7, 28] but the method is not necessarily reliable. It can be determined that a sampling device is unsatisfactory; in that event, the sample will be distributed throughout the system. However, the observation that no sample has gotten past the first trap does not guarantee that the collection has been quantitative, inasmuch as the sample may have decomposed or have been otherwise lost. The only reliable means for determining the collection efficiency of a sampling device is the use of a gas standard.

A sampling device of recent development that has not been applied to aldehydes is the passive monitor. The monitor consists of a diffusion tube containing a trapping agent at one end. The device is inexpensive and easy to use, expediting large-scale sampling. Palmes et al.[95] have been instrumental in developing the theory of passive monitors and successfully constructing a passive monitor for nitrogen dioxide.

TABLE 1

Collection Efficiencies of Various Trapping Solutions for Aldehydes

| Trapping Solution | Aldehyde | Collection Efficiency % | Calibration Method[a] | Iced | Reference |
|---|---|---|---|---|---|
| Water | Formaldehyde | 84 | A | No | 4, 9 |
| | | 85 | D | Yes | 85 |
| | | 80 | E | No | 130 |
| 1% Aqueous bisulfite | Formaldehyde | 100 | B | Yes | 137 |
| | | 94 | B | Yes | 74 |
| | Acetaldehyde | ∿100 | B | Yes | 74 |
| | Propionaldehyde | 100 | B | Yes | 137 |
| | | 96 | B | Yes | 74 |
| | n-Butanal | 100 | B | Yes | 137 |
| | | ∿100 | B | Yes | 74 |
| | i-Butanal | 100 | B | Yes | 137 |
| | | 98 | B | Yes | 74 |
| | n-Pentanal | 97 | B | Yes | 74 |
| 3-Methyl-2-benzothi-azolone hydrazone (MBTH) | Crotonaldehyde | 92 | B | Yes | 74 |
| | Formaldehyde | 88 | B | No | 28, 109 |
| | | 84 | C | No | 50 |
| | | 92 | E | No | 88 |
| | $CH_2CHO$ | 75 | C | No | 28 |
| | Propionaldehyde | 65 | C | No | 28 |
| Chromotropic acid in concentrated sulfuric acid | Formaldehyde | 99 | A | No | 7 |

Table 1 (continued)

| Trapping Solution | Aldehyde | Collection Efficiency % | Calibration Method[a] | Iced | Reference |
|---|---|---|---|---|---|
| Concentrated sulfuric acid | Formaldehyde | ∿99 | A | No | 7 |
| Hydroxylamine | Mixed | >90 | A | No | 132 |
| Dinitrophenylhydrazine (DNPH) | Mixed | ∿90 | A | No | 49 |
| Girard-T | Mixed | Good | E | No | 132 |
| Ethanol | Acrolein | 80-90 | A | Yes | 28 |
| Ethanol and 4-hexyl-resorcinol | Acrolein | 70-80 | A | Yes | 28 |

[a]Calibration methods: A, ratio of first impinger to total; B, syringe-pump evaporation of aldehyde solution; C, evaporation of aldehyde solution; D, use of headspace vapor over aldehyde solution; E, unknown.

## CONTINUOUS SAMPLERS

As stated earlier, there are direct investigative methods for determining the concentrations of compounds in situ, e.g., infrared and microwave spectroscopy. None of these methods has been rendered sufficiently portable to be used in field studies. The details of these methods and their potential future applications are discussed later in this chapter.

Several continuous analyzers based on wet chemical methods have been constructed.[24,80,140] These analyzers are intended to combine the best elements of direct and indirect sampling. Air is sampled via an impinger apparatus to generate a preconcentrated sample that, instead of being transported to a central laboratory for analysis, is analyzed in the field.

The continuous analyzer described by Yunghans and Munroe[140] and Cantor[24] is manufactured by Combustion Engineering Associates (CEA). The instrument can use the pararosaniline method to analyze for formaldehyde, or it can use the Purpald method to measure total aldehydes. One problem with this instrument is that it is not thermostatted. The color-development rate of pararosaniline is temperature-sensitive (Lahmann and Jander[69] and Miksch et al.[86]), and this may lead to erratic results. The impinger absorber coil is also sensitive to temperature fluctuations, because the collection efficiency of the absorbing solution and the amount that evaporates into the air stream depend on temperature. The mercury reagents used with the pararosaniline procedure are toxic. Finally, the recommended color-development time is too short to allow full color development that ensures maximal sensitivity and stability.

### WET-CHEMISTRY SPECTROPHOTOMETRIC ANALYSIS

Wet-chemistry spectrophotometric methods of analysis for aldehydes continue to be the most popular and widely used. The sensitivity associated with the formation of a dye chromophore and the ease of measurement with readily available spectrophotometers are not easily matched by other techniques. Field samples can usually be easily generated with simple equipment. However, spectrophotometric techniques are subject to error. The specificity and degree of completion of the chromophore-forming reaction must be considered, as well as the stability and standardization of reagents. In many cases, spectrophotometric techniques are slower than more direct measurement methods.

To sample air, wet-chemistry spectrophotometric methods are often applied to preconcentrated samples that are generated with impingers. It is often overlooked that the detection limit for aldehydes in air depends on both the sensitivity of the analytical method and the degree of preconcentration. If the time or flow rate is changed in sampling with impingers, the detection limit can be changed radically. Typically, aldehydes in air are sampled for 0.5-8 h at flow rates of 0.5-2.0 L/min.

TABLE 2

Summary of Spectrophotometric Methods for Formaldehyde Analysis in Ambient Air

| Method | Minimal Detectable Concentration | | $\lambda$max, nm | Interferences | Reference |
|---|---|---|---|---|---|
| | μg/ml | ppm (est.)[a] | | | |
| Chromotropic acid | 0.25 | 0.1 | 580 | Nitrogen dioxide, alkenes, acrolein, acetaldehyde, phenol, Formaldehyde precursors | 9, 130 |
| | 0.1 | 0.04 | 580 | | |
| Pararosaniline | 0.1 | 0.04 | 570 | Sulfur dioxide, cyanide | 86 |
| | 0.1 | 0.05 | 560 | Virtually specific | 80 |
| Phenylhydrazine | 1.1 | 0.4 | 520 | Color not stable | 82, 126 |
| J-acid (7-amino-4-hydroxy-2-naphthalene-sulfonic acid) | 0.3 | 0.1 | 468 | Formaldehyde precursors | 110 |
| Phenyl-J-acid | 0.4 | 0.13 | 660 | Formaldehyde precursors | 110 |
| p-Phenylenediamine | 1.7 | 0.5 | 485 | Sulfur dioxide, aliphatic aldehydes | 11 |
| Tryptophan | 0.15 | 0.06 | 575 | Virtually specific | 27 |
| MBTH | 0.05 | 0.015 | 628 | Higher aliphatic aldehydes | 111 |
| Purpald (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole) | 0.15 | 0.05 | 549 | Higher aldehydes | 59 |
| Acetylacetone | 1.4 | 0.5 | 412 | Specific (?) | 18 |

[a]Based on sampling at 1 slpm for 1 h into 25 ml of impinger solution and recording a difference of 0.05 absorbance unit between blank and sample.

## FORMALDEHYDE

To date, only spectrophotometric techniques have been applied in field studies of formaldehyde. Table 2 lists a variety of spectrophotometric techniques that can be used to analyze formaldehyde. The most widely used methods have been based on chromotropic acid, as tentatively recommended both in NIOSH[130] and in American Public Health Association Intersociety Committee.[9] Pararosaniline has been the next most popular reagent and may have some advantages over chromotropic acid. The remaining reagents have not been widely used. Some are inappropriate for field sampling, and others have not been adequately tested.

### Chromotropic Acid

Ever since Eegriwe[34] described the use of chromotropic acid in a spot-test method for the detection of formaldehyde, there has been widespread interest in using this reagent for spectrophotometric determination of formaldehyde. As stated above, a tentative method using this reagent has been suggested by both NIOSH[130] and the Intersociety Committee[9] for determining formaldehyde concentration in occupational environments.

The chromotropic acid method suggested by NIOSH and the Intersociety Committee involves the collection of samples by passage of air through two midget impingers in series, each of which contains 20 mL of distilled water. When a suitable volume of air has been sampled (1 h of sampling at 1 slpm), the contents of the midget impingers are analyzed separately. For analysis, the contents of an impinger are diluted quantitatively to a known volume. With 1% chromotropic acid, an aliquot of the sample is brought up to 0.025% chromotropic acid. Concentrated sulfuric acid is then added at 3 parts acid to 2 parts sample. The heat of mixing develops the color; after cooling of the sample, the absorbance is read at 580 nm (extinction coefficient, $\epsilon$, 8.9 x $10^3$).

The reported sensitivity of the method is 0.1 $\mu$g/ml of color-developed solution, which corresponds to formaldehyde at approximately 0.04 ppm in the sampled air (see Table 2). Acrolein is reported to be a positive interference at a few percent. Ethanol, higher-molecular-weight alcohols, and phenols can be negative interferences, but only at concentrations not normally encountered in the atmosphere. Olefins in tenfold excess over formaldehyde can be negative interferences of approximately 10%. Aromatic hydrocarbons also constitute a negative interference. With the exception of olefins, the interferences listed are not likely to be encountered in substantial concentrations during atmospheric sampling. Even in the case of olefins, the interference is not serious.[123]

Early work by Altshuller et al.[7] indicated that nitrogen dioxide did not interfere. However, the same cannot be said for nitrite and nitrate. Indeed, there is a chromotropic acid assay for nitrate similar to the formaldehyde assay.[135] Cares[25] was the first to investigate systematically the nature of the nitrite and nitrate interference and methods of eliminating it. She found that both interfered with formaldehyde analysis--nitrite slightly more than nitrate. When they were present in tenfold molar excess, negative interferences of 60% and 30%,

respectively were observed. Later work by Krug and Hirt[68] confirmed these findings. To overcome these interferences, Cares recommended a modified procedure that uses a solution of sodium bisulfite for sampling. This solution is neutralized and heated to reduce the oxides of nitrogen to nitric oxide, which outgasses from the solution. The sample is then analyzed as before, with chromotropic aid and sulfuric acid. This procedure has not been used in field studies, probably because of its complexity.

Oxides of nitrogen can probably interfere with analysis for formaldehyde with chromotropic acid. There is evidence that a major sink for $NO_x$ in the atmosphere involves its transformation to nitric acid (or its subsequent transformation to nitate-containing aerosols) by way of OH attached on nitrogen dioxide. Furthermore, nitrogen dioxide can be converted to nitrite and nitrate in the presence of water or sulfuric acid,[30] integral constituents of the analytic method.

It is not clear that the tentatively suggested method is optimized. Bricker and Johnson,[22] who originally developed a procedure using chromotropic acid, reported that full color development depended on heating of the reaction mixture for 30 min. Later work by West and Sen[136] and Altshuller et al.[7] suggested that the heat generated by the mixing of concentrated sulfuric acid with the sample solution was sufficient to drive the color-development reaction to completion. This conclusion is open to question, inasmuch as the peak temperature and duration of heating could be affected by the choice of reaction vessel and by the ambient temperature. Bricker and Johnson[22] also reported that the sulfuric acid concentration should be at least 67% for maximal color development. West and Sen,[136] however, reported that color development increased strongly with increasing sulfuric acid concentration until a value of 85% was reached, after which the dependence lessened. This finding was acknowledged by Altshuller et al.,[7] who went so far as to recommend that samples be collected with impingers containing chromotropic acid in concentrated sulfuric acid. Later simplex optimization work by Olansky and Deming[92] indicated that color development is maximal at 57% and declines at higher values.

In sum, it seems that the chromotropic acid method suffers from several deficiencies. It is not clear that the procedure is optimized for maximal sensitivity; the method suffers from interferences by a number of substances, some of which will undoubtedly be encountered during field sampling; and modifications designed to reduce these interferences introduce additional complexities.


Pararosaniline


A second reagent used for the measurement of formaldehyde concentrations is pararosaniline, which was first introduced in the form of a spot test by Schiff (1866).[114] In the classical Schiff test for aldehydes, the intense pink color of basic fuchsin is bleached with

sulfur dioxide in basic solution. When an aldehyde is added to the solution, it reverses the bleaching process, and the basic fuchsin color returns. This spot test is neither quantitative or formaldehyde-specific.

Lyles, Dowling, and Blanchard[80] were the first to develop a pararosaniline technique that produced a stable color and reproducible results. The technique is as follows. Samples are generated by passing air through a midget impinger containing distilled water. A reagent solution containing 0.05 M tetrachloromercurate II and 0.025% sodium sulfite is mixed with the sample in a ratio of 1 to 10. A second reagent solution, prepared by dissolving 0.16 g of pararosaniline and 24 ml of concentrated hydrochloric acid in water sufficient to total 0.1 L, is added to the sample in a ratio of 1 to 11. After 15 min, the absorbance is read at 560 nm.

Several aspects of this analysis require comment. Lyles et al. took note of earlier work [91, 134] and were careful to use pure pararosaniline in place of basic fuchsin reagent. The latter is often contaminated with rosaniline and is difficult to purify. Earlier problems with reagent stability and reproducibility may have resulted from insufficient purity.

The use of tetrachloromercurate II follows the work of West and Gaeke,[134] who used pararosaniline in conjunction with formaldehyde to determine sulfur dioxide. West and Gaeke sampled atmospheric sulfur dioxide by bubbling air through a solution of sodium tetrachloromercurae II. The sulfur dioxide was trapped and stabilized as a dichlorosulfitomercurate II complex, which then reacted with acidic pararosaniline and formaldehyde.

The pararosaniline method developed by Lyles et al.[80] is substantially the same as that used by the Combustion Engineering Associates (CEA) 555 continuous analyzer. The latter is used by many industrial hygienists to determine formaldeyde in workplace environments. Its primary virtue is its ability to give nearly real-time measurements.

Recent work has led to further refinements in the pararosaniline technique. Miksch et al.[86] took note of the work of Lahmann and Jander,[69] German workers who investigated the dependence of the technique of Lyles et al. on each of the reagents used. In particular, the stability and sensitivity of the method could be markedly improved through a fivefold reduction in the sodium sulfite concentration. Substantial temperature effects on both stability and time of development of the color were also noted.

In the same study, Miksch et al.[86] questioned the use of tetrachloromercurate II. Because the original role of this reagent had been to stabilize the sulfur dioxide collected in the procedure of West and Gaeke,[134] its function during formaldehyde determinations was not clear. Investigation revealed that reversing the order of addition of the reagents permitted the hazardous mercury reagent to be eliminated. No metal ion at all was found to be necessary.

The procedure developed by Miksch et al.[86] is as follows. Samples are collected in impingers containing deionized distilled water. The samples are collected, shipped back, and stored at 5°C to enhance sample stability before analysis. In the laboratory, the contents of two impingers operated in series are pooled, and the solution is diluted to a known volume. A reagent solution, prepared by dissolving 0.16 g of pararosaniline and 20 ml of concentrated hydrochloric acid in water sufficient to total 100 ml, is added to an aliquot of the sample in a ratio of 1 to 10. After 10 min, a second addition of 0.1% sodium sulfite solution is added to the sample in a ratio of 1 to 11. The reaction vessels are capped (to prevent outgassing of sulfur dioxide), and the color is allowed to develop for 1 h. The absorbance is then determined at 570 nm (extinction coefficient, $1.88 \times 10^4$).

The procedure is specific for formaldehyde. Only sulfur dioxide, an integral part of the procedure in the form of sulfite, constitutes a potential interference. This interference can be largely removed by basifying the impinger solutions with 1 or 2 drops of 1 N sodium hydroxide before analysis to destroy any formaldehyde-sulfur dioxide adduct. This allows ambient concentrations of sulfur dioxide up to 500 ppb--higher than normally encountered--to be tolerated. Miksch et al.[86] have reliably used the pararosaniline procedure in measuring several thousand indoor and outdoor air samples.

## Acetylacetone

A very sensitive fluorimetric method for the determination of formaldehyde is based on the Hantzsch reaction between acetylacetone (2,4-pentanedione), ammonia, and formaldehyde to form 3,5-diacetyl-1,4-dihydrolutidine. The reagent was first used in a colorimetric procedure by Nash,[90] who also reported that the adduct fluoresced. Belman[18] developed a fluorimetric procedure based on this property.

The procedure of Belman[18] is as follows: equal volumes of formaldehyde solution and a reagent consisting of 2 M ammonium acetate and 0.02 M acetylacetone (pH, 6) are mixed and incubated at 37°C for 1 h. After cooling to room temperature, the fluorescence is determined (excite = 410 nm, emit = 510 nm). The standard curve is linear with formaldehyde from 0.005 µg/ml to about 0.4 µg/ml and deviates slightly from linearity from 0.4 µg/ml to 1.0 µg/ml. Above 1.0 µg/ml, the formaldehyde can be determined colorimetrically.

This method has been particularly chosen by the wood industry in determining emission from particleboard and plywood.[19][84] Under controlled conditions in specially designed chambers, the formaldehyde content of headspace vapor over materials being examined is determined. This test is being considered for promulgation as a European standard.[107] Acetylacetone has not been used for sampling formaldehyde in ambient air. In this application, possible interference by oxides of nitrogen, sulfur dioxide, and ozone must be considered.[84]

Other Methods

It has already been mentioned that there are a large number of spec-
trophotometric methods for the determination of formaldehyde, in addi-
tion to the two discussed above. In general, these methods either have
not been fully evaluated or suffer from defects. Several alternative
wet-chemistry spectrophotometric methods of analysis are listed in Table
2. Closely analogous methods, based on spectrofluorometry, have also
been suggested, as shown in Table 3. One final analogous method deserv-
ing serious consideration is based on chemiluminescence. All these
methods are discussed below.

An older reagent that has been considered as a candidate for the
colorimetic determination of formaldehyde is phenylhydrazine. Reaction
of this reagent with formaldehyde, followed by oxidation of the adduct
with ferricyanide, leads to the formation of an anionic species absorb-
ing at 512 nm.[82] The essential drawback encountered is that color is
not stable and fades with time. Under some procedural conditions, ali-
phatic aldehydes interfere.[126] Other possible interferences have not
been investigated.

A reagent similar to chromotropic acid in both its structure and its
associated analytic technique is 7-amino-4-hydroxy-2-naphthalenesulfonic
acid (J-acid).[110] The adduct formed is fluorescent, and a second, more
sensitive, technique that takes advantage of this property has been
developed.[112] Formaldehyde precursors interfere under the harsh condi-
tions of both these techniques, and acrolein also interferes with the
second technique. Othr possible interferences have not been adequately
investigated. The reagent phenyl-J-acid is a minor modification of J-
acid.[110]

Two other reagents must be mentioned as potential candidates for the
wet-chemistry determination of formaldehyde, although they have not been
adequately tested. The reagent phenylenediamine may be oxidized by
hydrogen peroxide to produce Bandrowski's base, 3,6-bis(4-
aminophenylimino)cyclohexa-1,4-diene-1,4-diamine ($\lambda_{max}$, 485 nm). The
reaction is catalyzed by formaldehyde[11] and may form the basis for an
analytic procedure. At present, only sulfur dioxide in 100-fold excess
is known to interfere. The second reagent is tryptophan, which reacts
with formaldehyde in the presence of concentrated sulfuric acid and iron
to give a colored species.[27] The reaction was found to be extremely sen-
sitive and free of interference from a wide range of compounds, but its
suitability as a field sampling method has not been tested. The insta-
bility of some of the reagents used may present a problem.

Two final reagents have occasionally been used to assay for formal-
dehyde: 3-methyl-2-benzothiazolone hydrazone (MBTH) and 4-amino-3-
hydrazino-5-mercapto-1,2,4-triazole (Purpald). They are specific only
for the class of aliphatic aldehydes as a whole, and precautions must be
taken to ensure that separate formaldehyde is the only aldehyde present.
These reagents are discussed more fully in the next section.

Several workers have attempted to develop fluorometric methods of analysis for the determination of formaldehyde. The better known examples are shown in Table 3.

In general, the techniques are sensitive to the design of the instrument--note the different sensitivities reported for the same reagent at different time. The later work actually shows reduced sensitivity. Problems common to many fluorescence techniques are susceptibility to sample matrix variations and nonlinear standard curves. With the exception of acetylacetone, none of the reagents shown has been used in reported studies.

A final method deserving serious consideration is based on a chemiluminescent reaction of formaldehyde and gallic acid in the presence of alkaline peroxide.[122] In a flow system where the reagents can be mixed immediately before passage into an optical cell, formaldehyde concentrations as low as 3.0 ng/ml can be detected--an increase in sensitivity of more than an order of magnitude relative to the colorimetric procedures just described. A second distinct advantage is that the working linear range of response extends over five orders of magnitude.

The chemiluminescence method may not be completely formaldehyde-specific. Acetaldehyde was reported to give a response that was less than one-tenth that of formaldehyde. Other aldehydes were not tested. Two dicarbonyl compounds, glyoxal and methylglyoxal, gave a response equal in magnitude to that of formaldehyde.[128] These compounds would not normally be encountered, except perhaps in biological samples.

Proper design of the flow system and optical cell are essential to the chemiluminescence method. With proper design, the apparatus can be inexpensive. The method is best suited to analyzing aqueous impinger solutions at a central laboratory or to continuous monitoring at selected stationary sites.[52]

TABLE 3

Summary of Spectrofluorometric Methods of Analysis for Formaldehyde

| Method | Minimum Detectable Concentration | | $\lambda$excite, nm | $\lambda$emission, nm | Interferences | References |
|--------|------|------|------|------|------|------|
| | $\mu$g/ml | ppm[a] | | | | |
| 1,3-Cyclohexanedione | 0.2 | 0.7 | 395 | 460 | Higher aldehydes | 108 |
| Dimedone (5,5-dimethyl-cyclohexane-1,3-dione) | 0.08 | 0.03 | 470 | 520 | Higher aldehydes | 108 |
| J-acid (7-amino-4-hydroxy-2-naphthalene-sulfonic acid) | 0.6 | 0.1 | 470 | 520 | Aldehyde precursors, acrolein | 108 |
| J-acid | 0.05 | 0.02 | 470 | 520 | Aldehyde precursors acrolein | 110 |
| Acetylacetone | 1.2 | 0.4 | 410 | 510 | Specific (?) | 108 |
| Acetylacetone | 0.005 | 0.002 | 410 | 510 | Specific (?) | 18 |

[a]Based on sampling at 1 slpm for 1 h into 25 ml of impinger solution and recording a difference of 0.05 absorbance unit between blank and sample.

## TOTAL ALIPHATIC ALDEHYDES

Measurements of total aliphatic aldehydes are based on chemical reaction behavior imparted by the presence of the formyl group common to all aldehydes. As with formaldehyde, only wet-chemistry spectrophotometric techniques have been used for sampling total aliphatic aldehydes under field conditions. The application of more sophisticated instrumental techniques to the determination of total aliphatic aldehydes is inadvisable, because it is usually easier and more desirable to identify and measure each specific aldehyde separately.

### 3-Methyl-2-Benzothiazolone Hydrazone

By far the most commonly used reagent for the determination of total aliphatic aldehydes is MBTH. First introduced by Sawicki et al.,[111] this reagent has been used for measuring lower-molecular-weight aliphatic aldehydes in auto exhaust and urban atmospheres (see Table 2).

A tentative method using MBTH for determining aldehydes in ambient air was given by the Intersociety Committee.[9] The method is as follows. Air to be sampled is bubbled through 0.05% aqueous MBTH contained in a midget impinger. After dilution to a known volume, an aliquot of an oxidizing reagent containing sulfamic acid and ferric chloride is added. After 12 min, the absorbance is read at 628 nm. At the recommended sampling rate of 0.5 slpm, assuming a minimum detectable absorbance change of 0.05 unit, a concentration of 0.03 ppm could be determined after sampling air for 1 h.

The original method of Sawicki et al.[111] used ferric chloride alone as the oxidizing reagent. Because of turbidity, acetone was incorporated into the dilution scheme. Hauser and Cummins[50] effectively eliminated the turbidity by adding sulfamic acid to the oxidizing reagent. The molar absorptivities of the aldehydic adducts formed vary between approximately 48,000 and 56,000. The formaldehyde adduct has a molar absorptivity of 65,000. Altshuller et al.[2] recommended that concentrations of aldehydes determined by MBTH should be multiplied by a factor of 1.25 to account for the difference in response between formaldehyde and the remaining aliphatic aldehydes. The recommendation has not been followed in reported uses of MBTH.

May classes of compounds, particularly those containing nitrogen, react with MBTH to give colored products. Most of these compounds are not encountered during atmospheric sampling. Nitrogen dioxide has been reported to interfere through formation of nitrite and nitrate in water.

## Purpald

A reagent recently developed for the determination of aliphatic aldehydes is Purpald. First described by Dickinson and Jacobsen,[32] the reagent can be used quantitatively as follows.[59] A basic solution of Purpald is added to aqueous samples containing formaldehyde. The mixture is aerated for 30 min to ensure oxidation, and the absorbance is determined at 549 nm. Assuming that impingers are used for sampling air at a rate of 1 slpm for 1 h and that the minimum detectable absorbance difference is 0.05 unit, a concentration of 0.04 ppm can be detected. Purpald suffers from the same drawback as MBTH: it gives different responses to different aldehydes. Potential interfering substances encountered in atmospheric sampling have not been completely examined, but no interference from a wide variety of test compounds was noted by the originators.[32]

## Other Methods

2,4-Dinitrophenylhydrazine (DNPH) has received considerable attention as a reagent for determining aldehyde concentrations. The vast majority of DNPH techniques attempt to separate and identify the individual aldehydic adducts through the use of thin-layer chromatography, gas chromatography, or high-performance liquid chromatography. Wet-chemistry spectrophotometric procedures are based on the formation of a chromogen absorbing at 440 nm.[96, 101] These procedures have been hampered by the interference of ketones and problems with reagent stability. The minimum detectable concentration of aldehydes with these procedures is about 0.2 ppm.

A method deserving mention is the bisulfite method published by the Los Angeles Air Pollution Control District.[70] Air is sampled with impingers containing aqueous bisulfite. The aldehydes react to form aldehyde-bisulfite adducts. The excess bisulfite is destroyed, and the solution is basified to liberate the bisulfite bound in the adducts. The freed sulfite is titrated with iodine and starch. The method is cumbersome, the adducts are not stable for long periods even if kept on ice, and the iodine reagent is sensitive to air and light.

## ACROLEIN

Acrolein is a highly toxic aldehyde; a threshold limit value (TLV) of 0.1 ppm, has been established by the Occupational Health and Safety Administration (OSHA).[131] This standard is 30-fold lower than the corresponding TLV for formaldehyde. Acrolein is the only aldehyde other than formaldehyde for which there is a specific wet-chemistry spectrophotometric method of analysis.

### 4-Hexylresorcinol

The most popular method for determining acrolein in air uses 4-hexylresorcinol.[28, 65, 130] Air is typically drawn through two midget impingers at 1 slpm to collect the sample. The collecting solution can be either 1% sodium bisulfite or a reagent containing 4-hexylresorcinol, mercuric chloride, and trichloroacetic acid in ethanol. Samples collected in bisulfite are analyzed by adding 4-hexylresorcinol and mercuric chloride in ethanol and then a solution of trichloroacetic acid in ethanol. The solution is heated for 15 min at 60°C, and the resulting color is measured at 605 nm. Samples collected in 4-hexylresorcinol are analyzed simply by heating and measuring the color. For field sampling, the simplicity of the latter method is offset by the hazards of handling

the toxic and corrosive reagent. In addition, the reagent and the samples collected are not very stable, and samples must be analyzed within a few hours. The bisulfite method is somewhat more complex, but it is safer to use. Besides using a less hazardous collecting solution, this method produces samples that are stable for up to 48 h if they are kept refrigerated, thus permitting later analysis at a central laboratory.

A recent paper by Hemenway et al.[51] pointed out a potential flaw in the 4-hexylresorcinol method given by NIOSH.[130] Apparently, the order of addition of reagents for analysis differs between field samples and calibrating solutions, and this may lead to underestimation by as much as 35%. The validity of this objection needs to be established.

## Other Methods

Chromotropic acid has also been suggested for acrolein determination.[46] In the formaldehyde procedure using chromotropic acid, the response to acrolein is regarded as an interference; however, the absorbance maximums are sufficiently different that it is possible to measure the two compounds separately. A method for the simultaneous determination of formaldehyde and acrolein in air has been proposed by Szelejewska.[125] Samples are collected in bisulfite at 1 slpm before the addition of chromotropic acid reagent, the absorbance is measured at both 420 and 575 nm. The two absorbances are fitted to a linear system of two equations that, when solved, give the concentrations of the two aldehydes. This method has not been used in practice.

Two other reagents for the analysis of acrolein have been discussed by Cohen and Altshuller.[28] The first, phyloroglucinol, reacts with acrolein to produce a red color. The reaction is subject to interference from formaldehyde and oxides of nitrogen and has not ben used. The second, tryptophan, reacts with acrolein in acid solution to produce a purple color. The sensitivity of the tryptophan method is only one-fourth that of the 4-hexylresorcinol method. Furthermore, in view of the fact that a similar method has recently been used to determine formaldehyde,[27] the reagent may be subject to interference from formaldehyde.

## ACETALDEHYDE

The only colorimetric method reported to be specific for acetaldehyde uses diazobenzene sulfonic acid.[133] Unfortunately, no data are available on the sensitivity or interferences associated with this method. Some efforts have been made to take advantage of the rather high volatility of acetaldehyde, in separating it by distillation from other aldehydes. Procedures that use this method are too cumbersome to

be reliable. A method has recently been published for determining acetaldehyde in the presence of formaldehyde in biological materials.[31] Acetylactetone reacts with the solution, which eliminates the formaldehyde, and then the acetaldehyde is analyzed with p-phenyl phenol. This method does not take into account interferences from higher aldehydes; it is not actually a procedure for acetaldehyde, but rather for nonformaldehyde aldehydes. The only methods available for determining acetaldehyde involve the separation of all the aldehydes that are present with gas or liquid chromatography.

## OTHER ANALYTICAL METHODS

### SPECTROSCOPIC METHODS

Microwave, infrared, and laser-fluorescence spectroscopy have all been used to measure aldehyde concentrations in ambient air directly. Each of the methods is prohibitively expensive for ordinary field sampling. The instrumentation required is often cumbersome and delicate, is seldom portable, and requires sophisticated maintenance and support facilities.

Microwave rotational spectroscopy can measure low concentrations of many compounds in gas-phase samples. Rotational resonances are very sharp at microwave frequencies and low partial pressures, so sample spectra can be easily resolved. Formaldehyde has been monitored continuously at concentrations as low as 10 ppb in air with a two-stage membrane separator for preconcentration.[54] Acetaldehyde has been detected directly at 15 ppm.[55] This is far above normal concentrations for ambient air, and the technique is not routinely applicable to ambient-air analysis. Microwave spectroscopy has also been used to determine acrolein, acetaldehyde, and formaldehyde in tobacco smoke.[63] The sensitivity of the technique was reported to be 2 ppm, but, again, this concentration is rather high and would not normally be encountered in ambient air. Furthermore, the response time of the instrument is long, rendering the technique insensitive to changes in concentrations.

Infrared spectroscopy is promising, owing to the sharpness of the rotational and vibrational peaks observed for gas-phase samples. Unfortunately, good spectral resolution (less than 0.1 $cm^{-1}$) and rapid measurements are hampered by the low power of infrared sources. To overcome this difficulty, Fourier-transform infrared (FTIR) methods have been developed in which conventional Fourier-transform methods are used to derive the absorption bands. FTIR instruments are commercially available, but are exceedingly expensive. In one application, formaldehyde was continuously monitored at ambient concentrations of less than 10 ppb with an FTIR system.[128] The system used a Michelson infrared interferometer with a sophisticated multiple-reflection optical cell whose pathlength was 2 km. Longer pathlengths could not be obtained, because

of image overlap. Other aldehydes were not measured.

A fluorescence procedure based on the direct excitation of formaldehyde by a dye laser has been reported.[14] Formaldehyde as low as 50 ppb in air could be detected. The authors suggested that further refinements would increase the sensitivity. The application of this technique to other aldehydes is restricted by the weaker and less well-resolved absorption spectra in the accessible spectral region.


## CHROMATOGRAPHIC METHODS


Three chromatographic techniques have been applied to the analysis of aldehydes; gas chromatography, liquid chromatography, and ion chromatography. Gas-chromatographic analysis of aldehydes generally takes one of two forms: direct analysis by gas or solution injection and derivatization followed by analysis.

Formaldehyde presents special problems with respect to direct analysis by injection. In a flame ionization detector (FID), a universal detector widely used for quantitative work, formaldehyde decomposes and gives a very small response. Thermal conductivity detectors (TCDs) are less sensitive and respond only to very high concentratins of formaldehyde. An electron capture detector (ECD) has a limited linear response range and is sensitive only to conjugated carbonyl groups. The photoionization detector (PID) is reported to be sensitive to formaldehyde (HNU Company, Newton Upper Falls, Mass.), but appears to have some drawbacks. Specifically, a high-energy lamp is required to detect formaldehyde; this drastically reduces both the selectivity and the lifetime of the detector.[33]

In principle, it is possible to circumvent the insensitivity of the FID to formaldehyde by catalytically reducing formaldehyde to easily detectable methane.[29] Because hydrogen is required for the operation of the FID, the reduction is easily achieved by passing a mixture of the column effluent and hydrogen gas over a short bed of catalyst before introduction into the FID. Deposits of nickel, thorium, and ruthenium on fine-mesh glass beads have all been used successfully to reduce formaldehyde to methane. The lack of success in applying the technique to routine analysis of formaldehyde can be attributed to problems in choosing proper gas-chromatographic conditions. Apparently, it is difficult to pass formaldehyde through any of a variety of column-packing materials quantitatively.[23]

With the exception of formaldehyde, aldehydes may be analyzed by direct gas injection if concentrations are high enough. By using a six-port valve equipped with a 1-ml gas-sampling loop, aldehydes can be routinely detected with an FID at concentrations as low as 0.03 ppm without preconcentration (Analytical Instrument Development, Inc., Avondale, Pa.). It is important to recall, however, that gas chromatography excels at separation, but provides minimal identification. Ambient-air

samples often contain hydrocarbons, and their responses may overlap and obscure the aldehydic responses. Bellar and Sigsby[17] reported a complex automated gas chromatographic technique to analyze for $C_2$-$C_5$ aldehydes that avoided this problem. Hydrocarbons and aldehydes from an air sample flowed onto a cutter column, where the aldehydes were retained as the hydrocarbons were passed through and vented. The cutter column was then backflushed to a cryogenic trap, where the aldehydes were reconcentrated before introduction onto an analytic column. About an hour was required for a complete analysis. The method has not been used by other workers.

Preconcentration before direct analysis has also been investigated. Pellizzari[99, 100] has reported the collection of some higher-molecular-weight aldehydes on Tenax-GC. After thermal desorption and reconcentration in a cryogenic trap, analysis is performed by gas chromatography/mass spectrometry. The method provided poor quantification. Gold et al.[45] successfully captured acrolein on molecular sieves. The sieves were desorbed with water, which was then injected onto a column packed with hydrophobic Tenax-GC. The method has not been used by other workers.

Derivatization is an alternative technique that has been extensively investigated. Levaggi and Feldstein[74] introduced a method in which samples were collected with impingers containing 1% sodium bisulfite solution. Aldehydes react with the bisulfite to form adducts. Formaldehyde and acrolein are analyzed by chromotropic acid and 4-hexylresorcinol methods, respectively. To analyze the remaining aldehydes, the bisulfite solution is injected onto a packed column in a gas chromatograph. Samples must be kept cold to prevent deterioration. The Intersociety Committee[9] has adapted the technique as a tentative method for the $C_1$-$C_5$ aldehydes, but there are no reported uses in the literature. A problem not explicitly discussed is the rapid degradation of column performance due to the in situ production of sulfur dioxide and sodium hydroxide as the adduct thermally decomposes.

Much work has been aimed at using 2,4-dinitrophenylhydrazone (DNPH) derivatives of aldehydes, well known for many years for their use in the qualitative identification of aldehydes. DNPH reacts with aldehydes in aqueous solution to form precipitates. In most attempts, this precipitate is redissolved in an organic solvent, which is then injected into a gas chromatograph. The resulting chromatograms show double peaks for each derivative corresponding to the syn- and anti-isomers formed around the nitrogen-carbon double bond characteristic of the derivative. These peaks are not symmetrical, because of steric influences during formation of the derivative. The peaks observed for the derivatives of propionaldehyde, acrolein, and acetone overlap and are difficult to separate. The most consistent problem is the verification that quantitative derivatization of the available aldehydes has occurred.

DNPH was applied by Hoshika and Takata[53] to the analysis of automobile exhaust and cigarette smoke. Papa and Turner[97, 98] also applied it to automobile exhaust. In a two-step process, preliminary separation of DNPH aldehyde derivatives by preparative gas chromatography was followed by analytic gas chromatography.[124] In analyzing food samples, a number

of workers have used glutaric acid and flash-exchange gas chromatography to regenerate free aldehydes from DNPH derivative.[47, 48, 62, 64, 76, 103]

A variety of alternative derivatizing reagents have been investigated. Gas chromatography of aldehydic derivatives of phenylhydrazine[67] and 2,4,6-trichlorophenyl hydrazine[61] have been studied. These reagents are close analogs of DNPH. The aldehydic derivatives of dimethylhydrazine,[60] hydroxylamine,[132] and tetramethyl ammonium acetyl hydrazide (Girard-T Reagent)[41, 42, 93] have been analyzed with gas chromatography. Like DNPH, these reagents all involve reaction of a free amine with the formyl group to form a nitrogen-carbon double-bonded derivative.

Direct analysis of aldehydes with high-performance liquid chromatograph (HPLC) has not been thoroughly investigated, primarily because of the lack of a detector with sufficient sensitivity. To circumvent this problem, aldehydes can be made to react with DNPH to form a derivative with a strong ultraviolet absorption spectrum. This approach has been investigated by Carey and Persinger,[26] Mansfield et al.,[81] Selim,[120] and others.

Ion chromatography is a new technique (DIONEX, Inc., Sunnyvale, Calif.) that has application to formaldehyde analysis. It combines liquid chromatography with an ion-exchange column to separate charged species. A conductivity detector provides excellent sensitivity. Formaldehyde is captured on specially impregnated charcoal and then desorbed with aqueous peroxide. The resulting formate ion can then be analyzed by ion chromatography. Two difficulties with the method are ensuring quantitative recovery of formaldehyde from the charcoal and preventing the peroxide reagent from oxidizing other materials to formate ion.

ELECTROCHEMICAL METHODS

In addition to the usual techniques of analyzing organic materials, aldehydes can be analyzed by electrochemical methods. Both polarographic methods and amperometric titrations have been used.

Lupton and Lynch[79] developed polarographic techniques for the analysis of aldehydes in a wide range of samples. McLean and Holland[83] adapted their technique to a portable system for rapid analysis of aldehydes in automotive exhaust sampled by bubbling into water. The polarograph was rendered portable by replacing the dropping mercury electrode with a quiescent mercury pool a few millimeters in diameter. Analysis used the method of standard additions. The procedure is not specific, however, even for aldehydes. The authors suggested differential-pulse polarography for separation of the aldehydes, but this has not been tested.

Ikeda[58] developed a short-circuit argentometric amperometric titration for determining formaldehyde with a rotating platinum electrode. Equimolar amounts of acetaldehyde produced substantial interference, and other aldehydes may as well. The method is suitable for measuring quantities of formaldehyde as low as 0.1 mg.


## CURRENT APPLICATIONS OF ANALYTICAL METHODS


The standard techniques for analysis of aldehydes in use today were developed for application in specific sampling situations. These situations and the techniques used are discussed below.


## AMBIENT AIR


The wet-chemistry spectrophotometric methods of analysis have been used extensively for the analysis of aldehydes in ambient air. The method based on MBTH has been applied to studies of total aliphatic aldehydes in the ambient atmosphere and from emission sources.[4, 6, 102, 117] As mentioned earlier, it has been recommended for the determination of total aliphatic aldehydes by the Intersociety Committee.[9]

Invariably in atmospheric or emission samples the principal aldehyde detected is formaldehyde. The most extensively used procedure is based on chromotropic acid.[5-7, 111, 117] The Intersociety Committee[9] and NIOSH[130] have recommended the use of chromotropic acid. Schiff's reagent (basic fuchsin) and pararosaniline also have been suggested for atmospheric determinations.[69, 80, 104]

The high toxicity of acrolein has prompted analyses of this aldehyde in atmospheric and emission samples. The only sufficiently sensitive colorimetric method available for analysis of acrolein is based on 4-hexylresorcinol,[1, 28] a reagent that has been used[6, 106, 117] and is recommended by the Intersociety Committee.[9] A single investigation used a gas-chromatographic technique to determine acrolein in ambient air.[17]


## GASOLINE AND DIESEL EXHAUST


The MBTH technique has been applied to automobile (gasoline)[118, 119] and diesel[105] exhaust emission to determine the concentration of total aliphatic aldehydes. Two titimetric procedures have also been used for auto-exhaust measurements.[36]

The chromotropic acid method has been used widely for measuring formaldehyde in automobile[3-5, 7, 71, 111, 119] and diesel[13, 37, 77, 78] exhaust. The Schryver method, involving the reaction of formaldehyde with phenylhydrazine followed by oxidation with potassium fericyanide to form a red derivative, also has been used in studies of formaldehyde emitted in automobile and diesel exhaust.[35, 36]

The acrolein content of automobile exhaust has been determined with the 4-hexylresorcinol method.[2, 12, 28, 71] Diesel-exhaust emission has also been studied with this technique.[13, 77, 78, 105]

Because of the relatively high concentrations of acrolein encountered in automobile and diesel exhaust, this pollutant can be effectively measured by gas-chromatographic techniques. Acrolein has been determined directly and as a derivative.[17, 37, 38, 56, 57, 118]


NONOCCUPATIONAL INDOOR AIR


Interest in measuring aldehyde concentrations in nonoccupational indoor environments is a relatively recent phenomenon. Workers in Europe were among the first to determine aldehyde and formaldehyde concentrations in residence. In the United States, attention has been focused on formaldehyde emitted from urea-formaldehyde products used in the construction of homes, especially mobile homes. Table 4 summarizes the studies performed to date.

Formaldehyde concentrations were determined for residences in Denmark,[10] the Netherlands, and the Federal Republic of Germany.[139] Maximum concentrations observed in European dwellings reached 2.3 ppm, but average concentrations were 0.4 ppm or less.[10, 139] Interestingly, maximum formaldehyde concentrations in residences built without formaldehyde-releasing materials in the Netherlands reached only 0.08 ppm, and average concentrations were only 0.03 ppm.[139] Chromotropic acid was used most often in these European studies.

The MBTH technique was used to measure total aliphatic aldehydes in a pair of mobile homes and a sample residence in Pittsburgh.[89] Breysse[21] used the chromotropic acid method recommended by NIOSH to sample 608 mobile homes in the state of Washington in which residents had complained of irritation; the peak formaldehyde concentration observed in an occupied home was 1.77 ppm, and the mean was less than 0.5 ppm. Garry et al.[43] used the chromotropic acid method with a shortened sampling time to assess formaldehyde concentrations in Minnesota mobile homes. The state of Wisconsin also has used the chromotropic acid method to sample in mobile homes in which residents had registered complaints.[138]

TABLE 4

Summary of Aldehyde Measurements in Nonoccupational Indoor Environments

| Sampling Site | Concentration,[a] ppm | | Method of Analysis |
| --- | --- | --- | --- |
| | Range | Mean | |
| Danish residences[10] | 1.8 (peak) | -- | Unspecified |
| Netherlands residence built without form-aldehyde-releasing materials[139] | 0.08 (peak) | 0.03 | Unspecified |
| Residences in Denmark, Netherlands, and Federal Republic of Germany[139] | 2.3 (peak) | 0.4 | Unspecified |
| Two mobile homes in Pittsburgh, Pa.[89] | 0.1-0.8[b] | 0.36 | MBTH bubblers |
| Sample residence in Pittsburgh, Pa.[89] | 0.5 (peak)[b] | 0.15 | MBTH bubblers |
| Mobile homes register-ing complaints in state of Washington[21] | 0-1.77 | 0.1-0.44 | Chromotropic acid (single impinger) |
| Mobile homes register-ing complaints in Minnesota[43] | 0-3.0 | 0.4 | Chromotropic acid (30-min sample) |
| Mobile homes register-ing complaints in Wisconsin[138] | 0.02-4.2 | 0.88 | Chromotropic acid |
| Public buildings and energy-efficient homes (occupied and unoccupied)[75] | 0-0.21 | -- | Pararosaniline and chromotropic acid |
| | 0-0.23[b] | -- | MBTH bubblers |

[a] Formaldehyde, unless otherwise indicated.

[b] Total aliphatic aldehydes.

Systematic studies of formaldehyde and total aliphatic aldehydes as pollutants in nonoccupational indoor environments have been performed by the Lawrence Berkeley Laboratory (LBL) (Lin et al.[75] and Miksch et al.[86] LBL has used the MBTH tecnique to determine total aliphatic aldehyde concentrations, and the chromotropic acid technique and a modified pararosaniline technique have been used to measure formaldehyde. Sampling sites have included conventional and energy-efficient homes (occupied and unoccupied) and public buildings, such as schools, office buildings, and hospitals.

## OCCUPATIONAL INDOOR AIR

Only occupational air-quality formaldehyde standards are recommended or promulgated by several agencies and professional organizations in the United States. OSHA[131] has promulgated an 8-h time-weighted average (TWA) standard of 3 ppm. The American conference of Governmental Industrial Hygienists[8] has promulgated a threshold limit value (TLV) standard of 2 ppm. NIOSH[129] has recommended an exposure standard of no greater than 1 ppm for any 30-min sampling period.

The Intersociety Committee,[9] of which the ACGIH is a member, and NIOSH[130] both recommend a method of analysis for formaldehyde based on the use of chromotropic acid. Despite this recommendation, workers investigating formaldehyde concentrations in occupational environments have used a variety of techniques summarized in Table 5.

Shipkovitz[121] investigated formaldehyde in textile plants where fabric was treated with formaldehyde-containing resins. Samples were generated by drawing air through bubblers containing sodium bisulfite solution and were analyzed by iodometric titration. The method was reported to have a sensitivity of 0.5 ppm, but was not specific for formaldehyde.

Collection in sodium bisulfite had been used earlier by the California Department of Public Health[20] to analyze air at a textile garment factory. The method of analysis was not reported. In the same year, however, the California Department of Public Health investigated airborne formaldehyde in a clothing store by using midget impingers containing a solution of MBTH.[87] As with sodium bisulfite, this reagent is not specific for formaldehyde.

A modified chromotropic acid procedure was used by Schuck et al.[115] to determine formaldehyde concentrations during a study of the ocular effects induced by smog components. Subjects were exposed to formaldehyde in a smog chamber. Chromotropic acid was used to determine formaldehyde concentrations between 0.04 and 10.9 ppm at two laminating plants using phenol-resorcinol glues.[40] A survey of six funeral homes used a modified chromotropic acid procedure, in which air was bubbled into 0.1% chromotropic acid in concentrated sulfuric acid, to determine exposure to formaldehyde during the embalming process.[66] Reported

concentrations of 0.09-5.26 ppm may have been in error on the high side, inasmuch as no prefilter was used on air-sampling lines to remove paraformaldehyde dust which was also present.

## TABLE 5

### Formaldehyde Measurements in Occupational Environments

| Sampling Site | Concentration[a], ppm | | Method of Analysis |
|---|---|---|---|
| | Range | Mean | |
| Textile plants[121] | 0-2.7 | 0.68 | Sodium bisulfite, iodometric titration |
| Garment factory[20] | 0.9-2.7 | -- | Collection in sodium bisulfite solution |
| Clothing store[87] | 0.9-3.3[b] | -- | MBTH bubblers |
| Smog chamber[115] | 0.01-unk | -- | Chromotropic acid |
| Laminating plants[40] | 0.04-10.9 | -- | Chromotropic acid |
| Funeral homes[66] | 0.09-5.26 | 0.25-1.39 | Chromotropic acid |

[a]Formaldehyde, unless otherwise indicated

[b]Total aliphatic aldehydes

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