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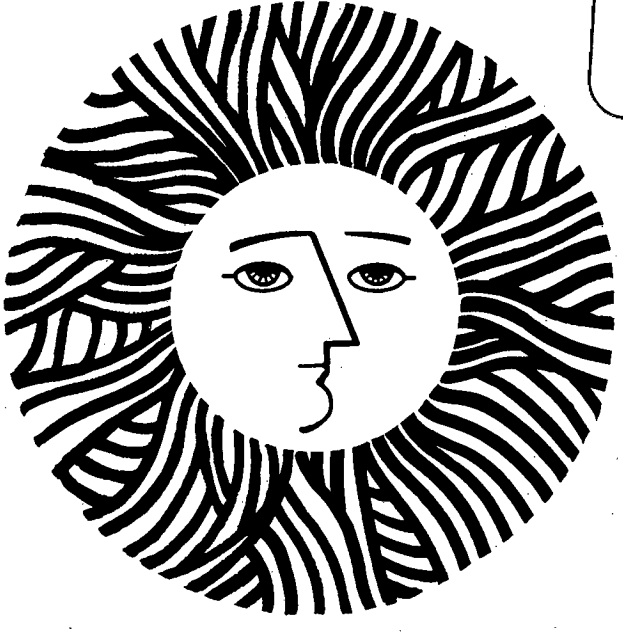

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ABSTRACT

A modified pararosaniline colorimetric method for more precise determination of formaldehyde in aqueous solution is described. Unlike earlier methods, the use of a hazardous mercury reagent is not required. The optimization of reagent concentrations, the effect of varying temperature, and potentially interfering compounds are reported. Comparative data on the analysis of aqueous formaldehyde solutions shows that the modified pararosaniline method is more sensitive, more reproducible, and easier to use than the widely accepted chromotropic acid method. The slopes of the calibration lines are 0.533 $AUmL\mu g^{-1}$ (absorbance units per microgram per milliliter) for pararosaniline and 0.233 $AUmL\mu g^{-1}$ for chromotropic acid. The percent errors for single determinations of formaldehyde solutions giving an absorbance of 1 are 1.1 and 3.1%, respectively, at the 95% confidence level. Both methods were used to determine indoor formaldehyde levels in two energy efficient homes, and the findings are compared.

KEYWORDS: formaldehyde, pararosaniline, chromotropic acid, indoor air pollution.

INTRODUCTION

There has been a great deal of interest recently in measuring atmospheric formaldehyde, particularly in non-industrial indoor environments, where the outgassing of formaldehyde from various products such as particleboard, plywood, and urea-formaldehyde foam insulation can cause irritation and potential harm to occupants (1-3). The U.S. Consumer Product Safety Commission has complied a large number of such complaints and is actively investigating the possible adverse health effects arising from exposure to formaldehyde (4). Investigations of formaldehyde levels in non-industrial indoor environments have relied on the analytical method commonly used for occupational settings (1-3,5,6), where the permissible exposure limit of 3 ppm (7) is more than three times that commonly encountered (2,5,6).

At the Lawrence Berkeley Laboratory (LBL) we have been measuring formaldehyde levels in energy-efficient homes and buildings as part of a program to determine the relationship between indoor air quality and the implementation of energy-conservation strategies (8). Our initial analyses used the recommended method which employs aqueous bubblers for sampling air and chromotropic acid for subsequent analysis (9,10); however, we found it to be insensitive and potentially subject to numerous interferences, by both inorganic and organic compounds (9-12), which could cause the results to be imprecise and erratic. Furthermore, the chromotropic acid method requires the use of hot concentrated sulfuric acid, which is difficult to work with.

Among the alternate reagents we considered, pararosaniline seemed promising. As early as 1866, Schiff (13) reported that the color of an SO_2 - bleached fuchsin solution was regenerated upon the addition of an aldehyde. Over the years, numerous attempts were made to develop quantitative assays for sulfur dioxide using this reaction (14-20) in combination with formaldehyde. The definitive work in this area was reported by West and Gaeke (21) who used sodium tetrachloromercurate (II) as an absorber to collect sulfur dioxide, and pararosaniline instead of fuchsin (an impure mixture of pararosaniline and rosaniline) for analysis. The West-Gaeke method was established as an international reference method (22) and, despite the advent of more sophisticated techniques, is still widely used because it is simple, sensitive, specific, and inexpensive.

In subsequent years several investigators developed a reliable assay for formaldehyde using pararosaniline and following the work of West and Gaeke (21). Lyles et al (23) reported a procedure in which a mercury (II) - sulfite reagent and an acidified pararosaniline reagent were sequentially added to an aqueous formaldehyde solution. Later work by Lahmann and Jander (24) modified the reagent concentrations to enhance sensitivity. A method derived from the above work is used today in commercially available automated analyzers (25).

Our major objection to the use of pararosaniline for determining formaldehyde was based on the need to handle toxic quantities of mercury. Since the original role of the mercury reagent in the procedure of West and Gaeke (21) had been to collect sulfur dioxide, it appeared possible to eliminate this toxic reagent without adversely affecting the

analysis of formaldehyde. Our studies showed that the mercury could be eliminated by reversing the order of addition of reagents.

This paper presents a modified pararosaniline colorimetric method for the determination of formaldehyde in aqueous solution that is more reproducible, more sensitive, more specific and easier to use than the widely accepted chromotropic acid procedure. The optimum reagent concentrations are established, and the need for hazardous mercury is eliminated. The modified pararosaniline method and the chromotropic acid method are applied to the determination of indoor formaldehyde levels in two homes, and the findings are compared. The structure of the pararosaniline chromophore and the reaction mechanism are discussed in view of the modifications implemented.

EXPERIMENTAL

Apparatus. Spectrophotometric measurements were made with a Varian Cary Model 219 spectrophotometer. Disposable 10 mm pathlength polystyrene cuvettes were used. Temperature was controlled with a Formatemp Junior (Forma Scientific) thermostated water bath.

Reagents. Pararosaniline (free base) was purchased from Sigma Chemical Company and paraformaldehyde from Eastman Chemical Company. All other chemicals used were analytical or reagent grade and were used without further purification. Methanol-free formaldehyde solutions were prepared by refluxing approximately 20 g of paraformaldehyde in water, filtering the solution, and diluting to 1.0 L. The solutions were standardized using the sulfite technique described by Walker (26), but substituting a pH meter for the original indicators. Thus, formaldehyde

was added to a 1 M solution of sodium sulfite to quantitatively produce sodium formaldehyde bisulfite and hydroxyl ions. The solution was then back-titrated to its original pH using 1.00 M HCl to determine the amount of formaldehyde added. The stock solution remained stable for several months. Dilute standards were prepared daily.

Pararosaniline Procedure. The concentrations of sulfite, hydrochloric acid, and pararosaniline were varied under the conditions of the optimized procedure reported here. For the optimized procedure two reagents are prepared. The first consists of 5 mM pararosaniline in 0.24 M HCl, which is prepared by dissolving 0.16 g of pararosaniline in 20 mL of concentrated HCl and diluting the mixture to 100 mL with deionized water. This reagent remains stable for several months when stored in an amber bottle. The second reagent is 8 mM sodium sulfite, prepared daily by dissolving 0.10 g of anhydrous sodium sulfite in deionized water sufficient to total 100 mLs.

To analyze a formaldehyde solution, 2.5 mL is placed in a cuvette and 250 µL of the acidified pararosaniline reagent is added. After mixing thoroughly, 250 µL of the sodium sulfite reagent is added. The cuvette is capped and the combined solution is again thoroughly mixed. The cuvette is placed in a water bath at 25 ^{o}C and the color is allowed to develop for 60 min. The absorbance is then read at 570 nm. The blank and the sample are read against deionized water.

Chromotropic Acid Procedure. For comparative studies the widely accepted procedure recommended by the APHA Intersociety Committee (9) was used with one modification. The amount of chromotropic acid was increased from 1% to 5% to insure full color development.

Field Samples. At the sites of interest visited by LBL, formaldehyde is sampled by means of a specially designed sampler constructed at LBL. The sampler consists of a small refrigerator that encloses four sampling trains, each of which has two polypropylene bubblers in series that contain 15 mL of distilled water. A detachable pump box (for noise control) draws air through the sampling trains, typically at 0.8 sLpm (standard liters per minute), for 12 to 24 hours. Flow control is achieved by using a constant differential flow controller (Moore Products Model 63 BU) to maintain a constant pressure drop across flow orifices, which are simple interchangeable hypodermic syringe needles. After sampling, the contents of the two bubblers in each sampling train are pooled and shipped back to LBL under ice in insulated containers. Sampling and shipping under ice are necessary to prevent serious deterioration of the samples.

For the field work reported here, the LBL formaldehyde sampler was used to sample indoor and outdoor air in two Oregon homes for approximately two week periods before and after energy conservation retrofitting (installation of storm windows and doors, weatherstripping, insulation of floors, ceilings, and ducts). Air was sampled for 24-hour periods from noon on one day until noon of the following day. At two-week intervals the samples were returned to LBL where they were analyzed using pararosaniline and chromotropic acid.

Ventilation rates were determined several times, before and after retrofitting, by a tracer gas technique (27). Sulfur hexafluoride was released into the indoor air and thoroughly dispersed with the aid of fans. Its disappearance with time was continuously monitored with a

Wilkes Model 102 infrared analyzer.

RESULTS AND DISCUSSION

Elimination of the Toxic Mercury Reagent. Lyles et al (23) and Lahmann and Jander (24) report procedures in which a mercury (II) - sulfite reagent and an acidified pararosaniline reagent are sequentially added to an aqueous formaldehyde solution. Attempts to directly substitute other metals for mercury were uniformly unsuccessful. However, it was found that the mercury could be eliminated merely by reversing the order in which the reagents were added. Identical results were obtained when calibration lines were prepared using the procedure of Lahmann and Jander, and when the order of reagent addition was reversed and a mercury-free sulfite reagent was used. This indicates that the mercury had no net effect on the reaction. Subsequent optimization and interference studies were performed on a procedure in which acidified pararosaniline and aqueous sodium sulfite are sequentially added to formaldehyde solutions.

Sensitivity of Pararosaniline Procedure as a Function of Reagent Concentration and Temperature. In order to determine how the concentrations of sodium sulfite and hydrochloric acid affect the sensitivity of the reaction, we analyzed a sample containing 1 $\mu g^{-1}mL$ (33 μM) formaldehyde and a blank containing only water over a wide range of acid and sulfite concentrations. The sensitivity (the difference in absorbance between the sample and the blank) is tabulated in Table I, while absorbance of the blank is shown in Table II. Figures 1 and 2, showing topographic presentations of the same data, were obtained by linear interpo-

absorbance of a blank was measured at the same time, and subtracted accordingly.

It can be seen that both the sensitivity and the development time are functions of temperature. The uncapped samples show the strongest dependence. The samples at 35 and 45 ^{o}C fade rapidly after 15 minutes, probably because of the evaporation of sulfur dioxide from the acidic solutions. The capped samples indicate that good results can be obtained for temperatures between 15 and 35 ^{o}C. If temperature control is used, a temperature near 25 ^{o}C will give the best results; however, if a calibration line is prepared with each set of analyses, room temperature will suffice.

Interferences. A number of compounds were tested to determine whether they interfered with the optimized pararosaniline procedure described above. In each case, water and a solution containing 1.0 μgmL^{-1} (33 μM) formaldehyde were made 1.0 mM in the potentially interfering compound and analyzed using pararosaniline. In this manner, both positive and negative interferences could be established. For compounds that gave an interference, this procedure was repeated until a concentration producing a 10% interference was established. For compounds that gave a positive interference, molar absorbtivities were established. The results are presented in Table III.

Only low molecular weight aldehydes gave positive interferences, and only when present in large excess over formaldehyde. Negative interferences could be caused by compounds that react with either pararosaniline or formaldehyde. Cyanide (27), sulfite (28,29) and hydroxylamine (30) all form stable, well-characterized adducts with formaldehyde.

It can be concluded that several common bubbler trapping agents such as sulfite, bisulfite, hydroxylamine, and semicarbazide cannot be used if subsequent analysis is to be done using pararosaniline.

Of the compounds tested, only sulfur dioxide and cyanide were thought to present a potential problem in air sampling applications. The interference arising from either of these compounds can be greatly reduced by returning to the original pararosaniline method (23,24) in which a mercury (II) - sulfite reagent is added to the sample prior to the addition of acidified pararosaniline. The mercury will complex with both the cyanide and the sulfite, decomposing the adducts and allowing the formaldehyde to react (see discussion on the Mechanism of Pararosaniline Reaction). For the method reported here, the interference by cyanide can be reduced by adding to the sample (in an amount sufficient to yield 10 mM) any of several metals that complex cyanide, including Hg(II), Cd(II), Ni(II), Fe(II), or Zn(II). The sulfite interference can be reduced by adding NaOH to the sample (in an amount sufficient to yield 0.1 M) prior to analysis. At high pH, the formaldehyde-bisulfide adduct decomposes and will not reform readily under the acidic conditions existing after the addition of the pararosaniline reagent (29,30).

Two gas phase interferences were also tested. Ozone (200 ppb) and sulfur dioxide (200 ppb) were added to air streams containing 50 ppb formaldehyde. The air was sampled for six hours at 1.0 sLpm using two impingers containing 20 mL of water connected in series in an ice bath. The zero air without O_3 or SO_2 was also sampled. Ozone did not produce any interference. Sulfur dioxide produced an interference nearly identical to that which would be produced by adding a comparable amount of

lation.

It can be seen from Figure 1 that the sensitivity takes the form of a ridge, and that the peak sensitivity occurs at low acid and sulfite concentrations. Unfortunately, as can be seen in Figure 2, the absorbance of the blank in this region is extremely high, making it unrealistic to try to make use of the most sensitive region of the curve. By selecting 0.10 absorption units as a reasonably low blank, the final hydrochloric acid concentration was fixed at 0.2 M (Figure 2). With this constraint, the final sulfite concentration was then chosen to be 0.8 mM by examining the area of maximum sensitivity in Figure 1.

Using the optimized concentrations of sulfite and hydrochloric acid thus determined, we examined the sensitivity as a function of pararosaniline concentration. The results are shown in Figure 3. It can be seen that the sensitivity increases somewhat with increasing pararosaniline concentration but that this increase is accompanied by an increase in the absorbance of the blank. It may be possible to increase both the acid and pararosaniline concentrations to obtain an acceptable value for the absorbance of the blank but, in so doing, the sensitivity would be reduced to about the same value as before. Thus, a final pararosaniline concentration of 0.5 mM (0.16 gL^{-1}), identical to that reported by Lahmann and Jander (24), was selected.

The effect of temperature on the color-forming reaction was investigated by analyzing a 1 μgmL^{-1} (33 μM) formaldehyde solution at different temperatures according to the optimized procedure. The samples were incubated both with and without caps. The absorbance of each sample was read every five minutes to produce the data shown in Figure 4. The

Na_2SO_3 to aqueous formaldehyde.

These results may be contrasted with those reported for chromotropic acid. The APHA Intersociety Committee (9) reports that saturated aldehydes give less than 0.01% positive interference, while acrolein gives a few percent positive interference. Presumably, the reported interference refers to equimolar concentrations of interferent and formaldehyde. Ethanol, higher molecular weight alcohols, olefins in tenfold excess, aromatic hydrocarbons and cyclohexanone are negative interferences. Phenol in eightfold excess results in a 10% to 20% negative interference. In addition to these interferences listed by the APHA Intersociety Committee (9), nitrite and nitrate have been shown to interfere (11,12). On this basis, it appears that pararosaniline exhibits superior selectivity relative to chromotropic acid.

Sensitivity and Reproducibility of Pararosaniline and Chromotropic Acid Methods. A series of calibration lines were prepared from common stock solutions using the chromotropic acid and pararosaniline procedures. Repetitive determinations were also performed on a blank sample, a sample containing 1.0 μgmL^{-1} formaldehyde, and solutions giving an absorbance of 1 (4.49 μgmL^{-1} for chromotropic acid and 1.80 μgmL^{-1} for pararosaniline). The results are given in Table IV.

The slopes of the calibration lines, 0.520 ± 0.037 (7%) $AUmL\mu g^{-1}$ (absorbance units per microgram per milliter) for pararosaniline and 0.233 ± 0.015 (6%) $AUmL\mu g^{-1}$ for chromotropic acid at the 95% confidence level, show that the pararosaniline procedure is more than twice as sensitive as the chromotropic acid procedure. The higher sensitivity of pararosaniline can have a substantial impact on the lower detection

limit reported in air sampling applications. For a 60 L sample of air (obtained by sampling for 1 hour at 1 sLpm as recommended by the APHA Intersociety Committee (9)), a concentration of 25 ppb can be determined using pararosaniline and 66 ppb using chromotropic acid. (This calculation assumes that there are 20 mL of absorbing solution and that a difference of 0.05 AU between the blank and the sample is recorded.)

The mean calculated intercept of the calibration line for pararosaniline, 0.099 AU, agrees closely with the mean determination of blank solutions, 0.093 AU. The corresponding values for chromotropic acid, 0.051 AU and 0.030 AU, do not agree as well, making the determination of low concentrations of formaldehyde difficult.

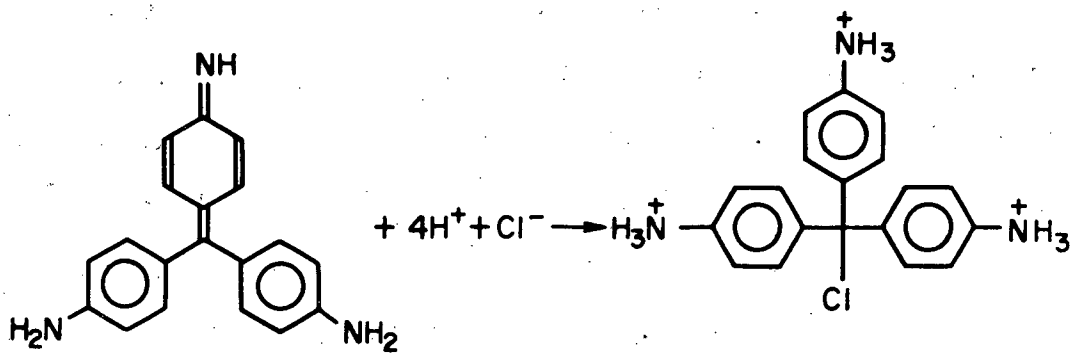
Single determinations of a blank solution, a solution of formaldehyde giving an absorbance of 1, and a solution of 1 μgmL^{-1} (33 μm) formaldehyde can be made using pararosaniline with relative errors of 4.3%, 1.1% and 2.2%, respectively, at the 95% confidence level. The corresponding relative errors (at the 95% confidence level) using chromotropic acid are 13%, 3.1% and 2.6%. Thus, pararosaniline shows greater reproducibility in every case.

Field Measurements. Table V shows indoor formaldehyde levels and ventilation rates determined at two Oregon homes before and after energy retrofitting. The mean formaldehyde levels, determined by applying the pararosaniline and chromotropic acid methods to a common set of aqueous formaldehyde field samples, are in good agreement (differences average less than 5%). The relative standard deviations of the mean levels also agree closely, but average 17%. The agreement in the mean levels is in accord with the reproducibility established for the two methods in the

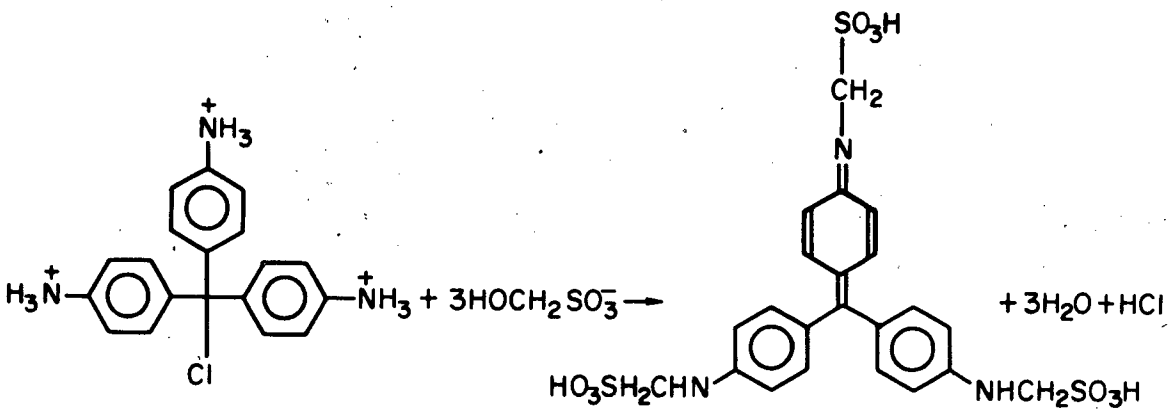
laboratory; however, the similarity and size of the relative standard deviation are in sharp discord.

These results can be reconciled if it is assumed that the variance among the collected field samples is substantially greater than the variance introduced during analysis with either the pararosaniline or chromotropic acid methods. Such variance could result from the manner in which field samples are collected or from true fluctuations in the indoor formaldehyde levels. The design of the LBL formaldehyde sampler makes the former explanation unlikely. If the reasonable assumption is made that indoor formaldehyde levels are dependent upon the rate at which indoor air is exchanged for relatively clean outdoor air, then variations in the exchange rate should result in changes in formaldehyde levels. As shown in Table V, the ventilation rates in these houses exhibit more than enough variance to account for the relative standard deviation of the mean formaldehyde levels. Though a portion of the variance must necessarily derive from the method of determination of ventilation rates, the majority, when measured in situ, reflects natural fluctuations in controlling variables such as temperature (inside and out), local windspeed, and occupant behavior. The reproducibility of indoor formaldehyde determinations is thus defined by the variance in the ventilation rate, not by the analysis procedure applied.

Mechanism of Pararosaniline Reaction. Nauman and co-workers (32) and Rumpf (33) studied the reaction and chromosphore in detail. Nauman stated that pararosaniline was decolorized in acid solution through the formation of an anilinium salt:

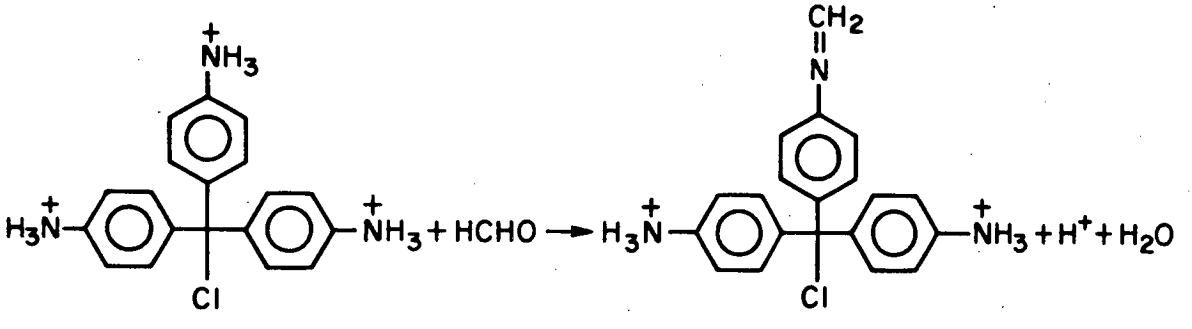


To develop a color, formaldehyde was added to the decolorized pararosaniline solution first, and sodium sulfite was added second. It was proposed that the first step in the color-forming reaction was the formation of the formaldehyde-bisulfite addition product. This compound then combined with the anilinium ion to form a sulfonic acid chromophore:

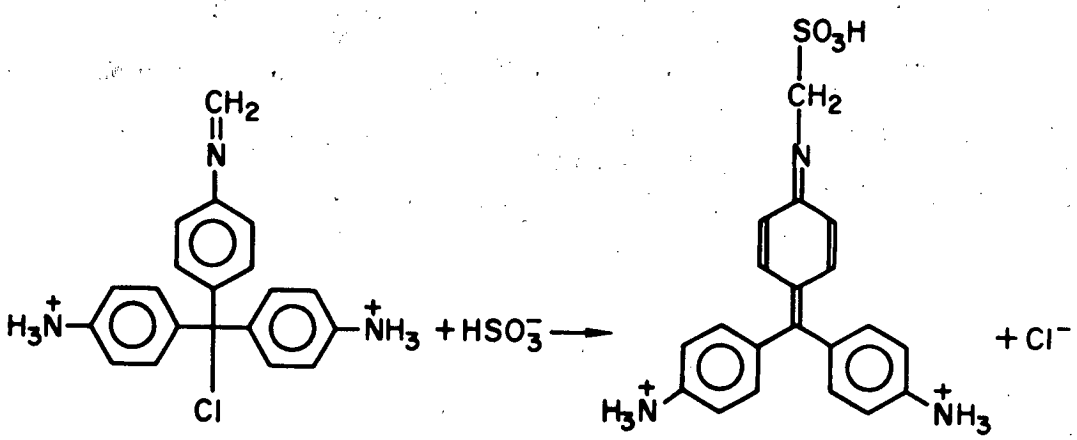


The color was assumed to appear as a result of the acid concentration not being strong enough to give a colorless anilinium-like salt of the sulfonic acid. (The degree of substitution was assumed to be threefold, as indicated.) Extensive kinetic studies by Skrabel and Skrabel (29), and Sorensen and Andersen (30) however, show that formaldehyde and sulfite react rapidly and quantitatively in neutral or basic solutions, but extremely slowly in acidic solutions. Furthermore, when a solution of sulfite is added to the formaldehyde sample first, and acidified pararosaniline second, no color develops. These findings contradict the mechanism proposed by Nauman.

When the order of addition is changed so that the formaldehyde and acid-bleached pararosaniline are mixed first, and the sulfide solution then added, color development occurs. The acidity of the resultant solution prevents the formaldehyde and sulfite from reacting and, presumably, the formaldehyde and pararosaniline react instead. A likely candidate for the adduct is a Schiff base:



This type of reaction is acid-catalyzed (34) and the product is likely to be stabilized by conjugation of the imine with the phenyl ring. The Schiff base, in turn, may combine with sulfur dioxide under acidic conditions to form an alkylsulfonic acid chromophore analogous to that proposed by Nauman et al (32):



The degree of substitution is assumed to be one since, under the conditions of the analytical procedure, pararosaniline is present in large excess. This reaction is analogous to the formation of a bisulfite addition product.

The assumption that a Schiff base is an intermediate prior to the formation of an alkylsulfonic acid has been refuted in a recent article by Dasgupta, et al (35). Citing the fact that the rate of color development changes depending on the order of addition of reagents, these workers argue for the participation of a carbinolamine intermediate. Unfortunately, their data cannot be used to argue conclusively for

either intermediate. Of greater importance is their conclusion that the final chromophore is an alkylsulfonic acid, as we believe.

It is instructive to consider the manner in which the use of a mercury (II)-sulfite reagent (23-27) allows the order of addition to be reversed. In neutral solution the mercury (II)-sulfite complex appears to be more stable than the formaldehyde-bisulfite adduct, and the latter compound does not form. Upon acidification by the addition of the pararosaniline reagent, the mercury (II)-sulfite complex decomposes to liberate sulfur dioxide. As noted, however, the acidity prevents the sulfur dioxide from reacting with the formaldehyde (29,30).

CONCLUSIONS

The optimized pararosaniline procedure described here for the determination of formaldehyde in aqueous solution is superior to the widely accepted chromotropic acid procedure. When determining formaldehyde in non-industrial indoor environments, its greater sensitivity allows sampling times to be shortened or reportable detection limits to be lowered. The elimination of the toxic mercury reagent makes it easier to use. It is also more reproducible and more specific, although these advantages were not a factor in determining the indoor formaldehyde levels reported in this work. The advantages of the pararosaniline method are significant enough to recommend broad-scale adoption of this method of determining formaldehyde in aqueous solution.

ACKNOWLEDGEMENTS

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Table I: Net Absorbance as a Function of the Final HCl and Sodium Sulfite Concentrations[a]

final Na_2SO_3 concentration, mM	final HCl concentration, mM								
	20	30	50	90	150	200	250	300	400
0.033	1.400	0.809	0.407	0.207	0.113	0.098	0.082	0.072	0.061
0.066	1.247	0.740	0.389	0.194	0.123	0.098	0.082	0.076	0.066
0.165	1.209	0.748	0.386	0.198	0.122	0.098	0.085	0.075	0.063
0.331	1.227	0.755	0.407	0.207	0.128	0.097	0.083	0.074	0.059
0.496	1.047	0.721	0.403	0.209	0.124	0.099	0.081	0.073	0.061
0.661	1.056	0.646	0.358	0.188	0.122	0.093	0.078	0.070	0.058
0.992	0.863	0.575	0.334	0.184	0.117	0.092	0.074	0.068	0.058
1.322	0.757	0.549	0.344	0.196	0.122	0.098	0.079	0.072	0.059
1.984	0.721	0.542	0.350	0.196	0.128	0.112	0.085	0.077	0.060
2.645	0.538	0.435	0.291	0.167	0.111	0.087	0.076	0.069	0.056
3.307	0.447	0.375	0.265	0.167	0.114	0.096	0.079	0.073	0.059
5.291	0.306	0.292	0.232	0.150	0.106	0.082	0.072	0.065	0.054
6.614	0.246	0.230	0.196	0.138	0.101	0.084	0.073	0.067	0.057

[a] All analyses were performed on a solution of 1.0 $\mu g mL^{-1}$ (33 μm) formaldehyde. The method of analysis was as described in the text. Each absorbance is the average of three determinations.

Table II: Absorbance of the Blank as a Function of the Final HCl and Sodium Sulfite Concentrations[a]

final Na_2SO_3 concentration, mM	final HCl concentration, mM								
	20	30	50	90	150	200	250	300	400
0.033	0.474	0.400	0.292	0.157	0.081	0.052	0.027	0.026	0.015
0.066	0.560	0.476	0.341	0.194	0.080	0.056	0.040	0.043	0.007
0.165	1.033	1.002	0.915	0.688	0.383	0.290	0.196	0.220	0.075
0.331	0.940	0.982	0.932	0.783	0.459	0.385	0.305	0.255	0.158
0.496	0.746	0.735	0.789	0.809	0.650	0.514	0.420	0.342	0.214
0.661	0.351	0.536	0.668	0.737	0.612	0.503	0.402	0.321	0.205
0.992	0.358	0.426	0.553	0.651	0.604	0.507	0.455	0.394	0.277
1.322	0.296	0.353	0.382	0.458	0.474	0.424	0.414	0.368	0.304
1.984	-0.014	0.038	0.125	0.275	0.337	0.354	0.342	0.342	0.291
2.645	-0.093	0.016	0.057	0.171	0.234	0.293	0.279	0.259	0.251
3.307	-0.023	0.029	0.071	0.145	0.227	0.266	0.274	0.259	0.254
5.291	-0.057	-0.030	-0.007	0.048	0.072	0.100	0.132	0.121	0.128
6.614	-0.085	-0.023	0.008	0.045	0.065	0.102	0.103	0.105	0.121

[a] All analyses were performed on a solution of 1.0 μgmL^{-1} (33 μm) formaldehyde. The method of analysis was as described in the text. Each absorbance is the average of three determinations.

Table III. Compounds Tested for Their Ability to Interfere with the Pararosaniline Procedure

	concentration necessary for 10% interference, μM[a]	molar absorptivity[b]
positive interferences:		
acetaldehyde	220	220
acrolein	120	390
propionaldehyde	640	77
glyoxal	500	130
negative interferences:		
sodium sulfite	12	
sodium sulfite (treated)[c]	220	
potassium cyanide	12	
postassium cyanide (treated)[d]	330	
sodium nitrite	120	
hydrogen peroxide	140	
hyroxylamine	3	

compounds giving less than 10% interference at 1.0 mM

- acetic acid
- acetone
- acetate anion
- bicarbonate anion
- n-butylaldehyde
- benzaldehyde
- ammonium cation
- ethanol
- methanol
- nitrate anion
- sulfate anion
- sulfide anion
- s-trioxane
- valeraldehyde

[a] Determined in the presence of 1.0 $\mu g mL^{-1}$ (33 μM) formaldehyde

[b] For comparison, the molar absorptivity of formaldehyde was determined to be 18,800.

[c] After treatment of sample with NaOH, as described in the text.

[d] After treatment with cyanide-complexing metal, as described in the text.

Table IV. Reproducibility of Pararosaniline and Chromotropic Acid Analysis Procedures for Formaldehyde

	calibration line[a]			repetitive measurements of solutions[b]		
	slope AUmLμg^{-1}[c]	intercept AU	$\bar{R}$	blank AU	formaldehyde to give abs near 1 AU[d]	1 μgmL^{-1} formaldehyde AU[e]
pararosaniline[f]	0.520 ± 0.015	0.099 ± 0.008	0.9967	0.093 ± 0.004	0.991 ± 0.005	0.605 ± 0.006
chromotropic acid[f]	0.233 ± 0.006	0.051 ± 0.007	0.9990	0.030 ± 0.004	1.166 ± 0.016	0.261 ± 0.003

[a] Line of best fit determined by method of least squares. Errors are expressed as relative standard deviation from mean, seven observations.

[b] Errors are expressed as relative standard deviation from mean, ten observations.

[c] Reproducibility of slopes: 0.520 ± 0.037 (7%) and 0.233 ± 0.015 (6%) at the 95% confidence level.

[d] Percent error (single determination) at a formaldehyde concentration giving an absorbance of 1 (1.80 μgmL^{-1} for pararosaniline and 4.49 μgmL^{-1} for chromotropic acid): 1.1% and 3.1% respectively for pararosaniline and chromotropic acid at the 95% confidence level.

[f] Method of analysis is as described in the text.

Table V. Formaldehyde Levels and Ventilation Rates Measured in Two Oregon Homes Before and After Retrofit

	ventilation rate[a]		average formaldehyde level, ppb[b]	
	Fan On	Fan Off	Pararosaniline	Chromotropic Acid
Medford 1 pre-retrofit	0.62 ± 0.25 (n=17)[c]	0.33 ± 0.14 (n=11)[c]	55 ± 9 (n=14)[c]	53 ± 9 (n=14)[c]
Medford 1 post-retrofit	0.49 ± 0.11 (16)	0.20 ± 0.08 (11)	53 ± 6 (10)	53 ± 0 5 (10)
Medford 2 pre-retrofit	0.82 ± 0.07 (8)	0.33 ± 0.08 (3)	68 ± 12 (11)	62 ± 14 (11)
Medford 2 post-retrofit	0.58 ± 0.14 (13)	0.2 ± 0.05 (6)	51 ± 10 (13)	54 ± 12 (13)

[a] Ventilation rates were determined using tracer gas techniques. "Fan on" and "fan off" refer to the operation of a central air conditioning unit. The unit was on for approximately six hours each day, between 6 P.M. and 12 P.M.

[b] Air was sampled continuously for 24-hour periods using the LBL formaldehyde sampler described in the text. The pararosaniline and chromotropic acid methods were applied to each sample. Outdoor levels, determined simultaneously, were all less than 5 ppb.

[c] Errors are expressed as relative standard deviations from the mean. The number in parentheses indicates the number of measurements made in each case.

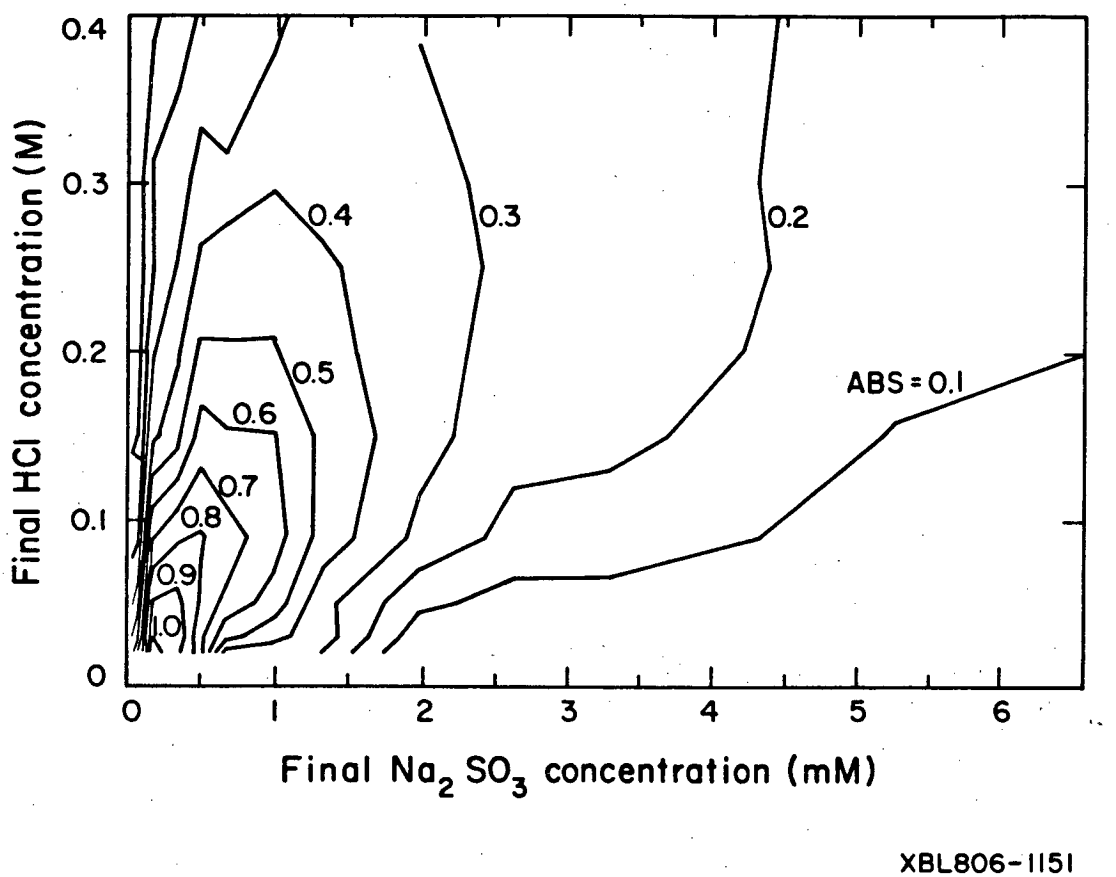

Figure 1. Net absorbance as a function of the final hydrochloric acid and sodium sulfite concentrations. All analyses were performed on a solution of 1.0 $\mu g\ mL^{-1}$ (33 μm) formaldehyde. Data shown were obtained by linear interpolation from the data given in Table I.

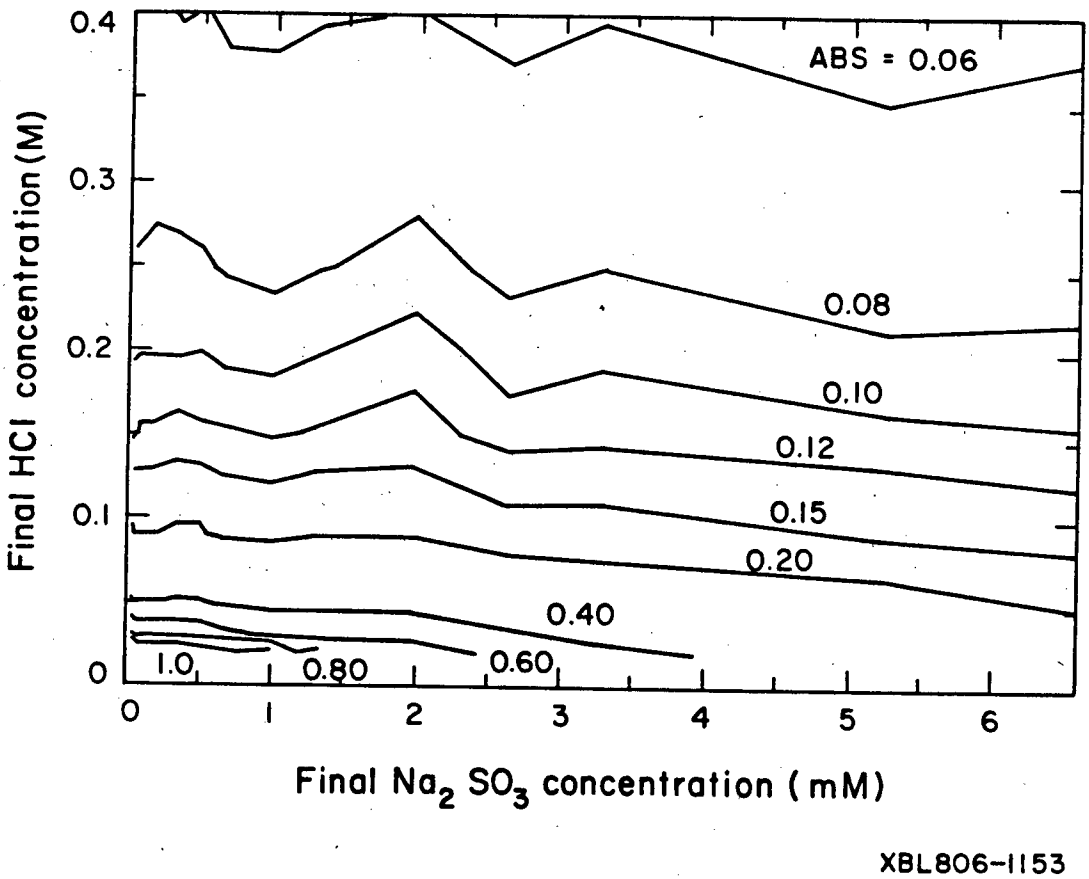

Figure 2. Absorbance of the blank as a function of the final hydrochloric acid and sodium sulfite concentrations. Data shown were obtained by linear interpolation from the data given in Table II.

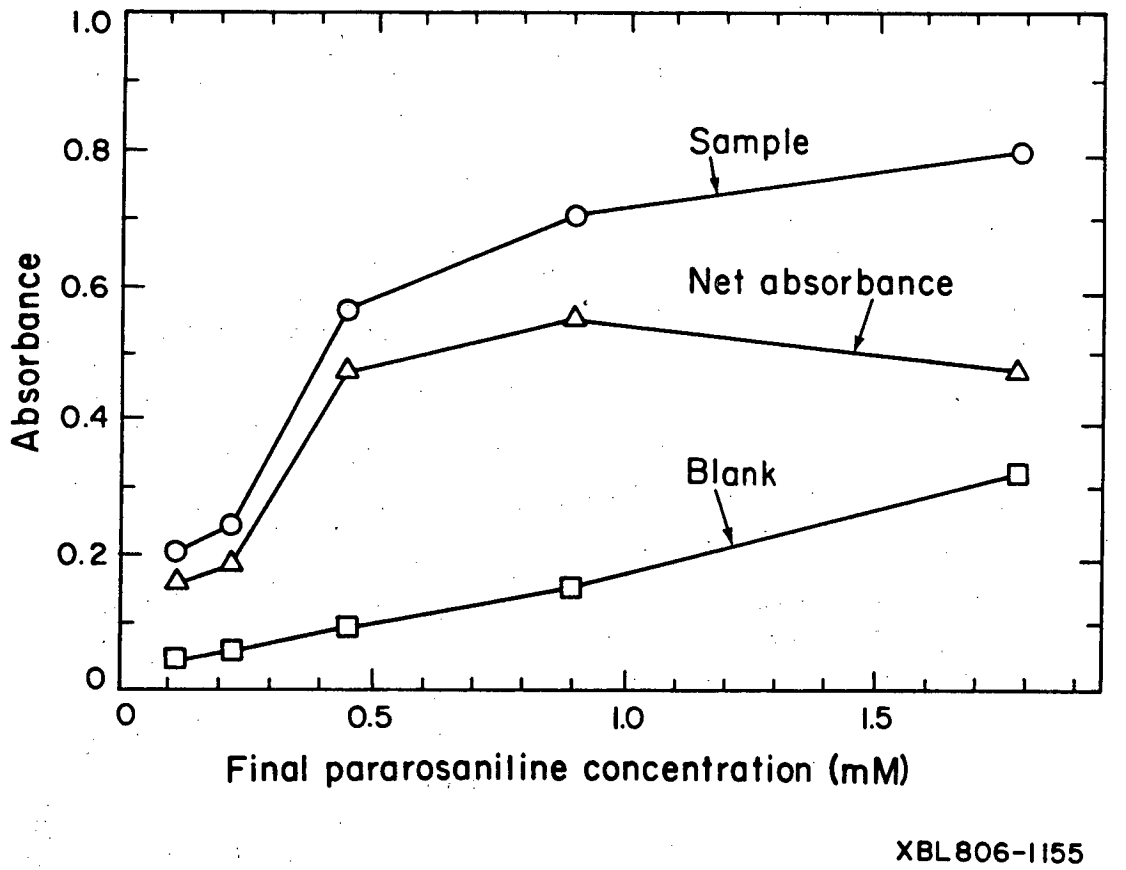

Figure 3. Absorbance as a function of the pararosaniline concentration. A sample of 1.0 $\mu g\ mL^{-1}$ (33 μm) formaldehyde and a blank were analyzed using pararosaniline and the optimized concentrations of hydrochloric acid and sodium sulfite.

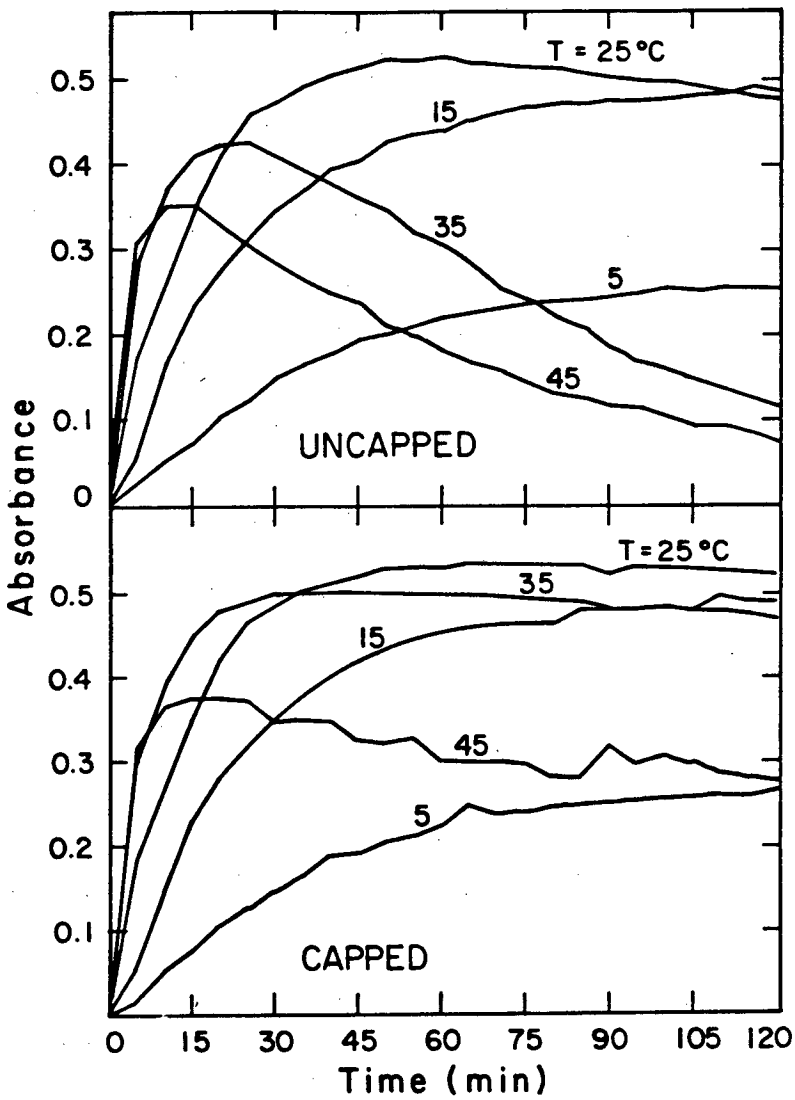

Figure 4. Net absorbance as a function of time at various temperatures: a) with cuvettes capped and b) with cuvettes uncapped. The optimized reagent concentrations were used.

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