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Test results using the NIOSH analytical method S21 for acrolein (107028) are reported. The procedure involves sample collection in a buffered Girard-T solution or in a midget bubbler charged with hydroxylamine solution, and analysis by differential pulse polarography. Analytical equipment and procedures are described along with generation of test atmospheres. Data on stability and recovery rate is included. The procedure using Girard-T reagent was unsatisfactory due to instability of the sample, and the collection efficiency of hydroxylamine was inadequate.

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Failure Report No. S21

October 28, 1977

Substance:	Acrolein
OSHA Standard:	0.1 ppm (0.25 mg/cu m)
Chemical Used:	Acrolein, 97%, with 200 ppm hydroquinone Aldrich Chemical Company

Methods Attempted

The first method studied was collection and derivatization of acrolein in a buffered Girard T reagent solution and analysis of the derivative by polarography. The second method attempted was collection of acrolein in a midget bubbler charged with hydroxylamine solution, and analysis of the resultant acrolein oxime by differential pulse polarography.

Reason for Failure

The method involving collection in Girard T reagent was not successful, because samples were not adequately stable. In the method employing hydroxylamine for the collection medium, collection efficiency was not adequate.

Introduction

There are several methods for the collection and analysis of acrolein. These include analysis by colorimetry and gas chromatography. In the colorimetric method, acrolein is treated with 4-hexylresorcinol which is present in the collection medium. Samples must be analyzed within two hours (Reference 1). In a modification of this method, acrolein is collected in a sodium bisulfite solution and later reacted with 4-hexylresorcinol. Cold storage is necessary (6°C) unless the color formation and analysis are performed within four hours (Reference 2). The collection efficiency is reported to be 70-80% using a single midget bubbler; therefore, the above method uses two midget bubblers connected in series.

In a method described by Hurley and Ketcham (Reference 3), hydroquinone-treated charcoal is used to collect the acrolein, which is then desorbed with ethylene dichloride, and analyzed by gas chromatography, using a 9% Carbowax 20M column. While gas chromatographic analysis provides separation of some interfering contaminants, collected samples must be analyzed the same day or refrigerated.

It was decided to develop a method which derivatized and stabilized acrolein during collection. The derivatization methods described below seemed to have the greatest potential for success.

Discussion

Method Using Girard T (GT) Derivative

The first method tested for acrolein was formation of a derivative by reaction with Girard T reagent, N,N,N-trimethylammoniumacetylhydrazine (GT). It was proposed that acrolein be collected in a midget bubbler containing a buffered aqueous solution of GT, and analyzed by polarography.

The reaction between GT and acrolein is shown in equation 1.

$$(CH_3)_3\overset{+}{N}CH_2CO\text{-}NHNH_2 + CH_2{=}CHCHO \overset{H^+}{\rightleftharpoons} (CH_3)_3\overset{+}{N}CH_2CONHN{=}CH{-}CH{=}CH_2 + H_2O \qquad (1)$$

This reaction is similar to that of unhindered aldehydes with a number of hydrazine derivatives such as semicarbazide and phenyl hydrazine (Reference 4). Studies by Conant and Bartlett (Reference 5) showed that the reaction is general acid catalyzed. The forward reaction is slow in alkaline solution, but high acidity promotes hydrolysis. It was attempted to find the optimum pH so that the reaction rate was fast enough to trap and preserve acrolein in the collection medium during sampling, and the reverse hydrolysis rate was at a minimum.

Various collection medium conditions were studied. The rate of derivative formation as a function of GT concentration was tested, holding the pH and acrolein concentrations constant. For these tests, an acrolein concentration of 5.22×10^{-5} M was used. The pH was 4.5, obtained by using a 0.4 M solution of NaH_2PO_4. Samples were analyzed by uv spectrophotometry and the absorbance measured at 260 nm as a function of time. Completion of the reaction was taken to be that time when no further increase in absorbance took place. Table S21-1 summarizes the results of this test.

Table S21-1

Reaction Time vs GT Concentration

Acrolein Concentration	GT Concentration	Time Until Completion
5.22×10^{-5} M	0.58×10^{-3} M	greater than 45 min
5.22×10^{-5} M	1.74×10^{-3} M	28 min
5.22×10^{-5} M	2.89×10^{-3} M	12 min
5.22×10^{-5} M	11.6×10^{-3} M	3 min
5.22×10^{-5} M	23.2×10^{-3} M	3 min

From these data, it was decided to use a solution that was at least 11×10^{-3} M in GT. This would represent a greater than 200-fold molar excess of GT over acrolein, assuming that samples were to be taken for 2 hours at 1 liter/minute in 10 mL of solution, and acrolein was present at the OSHA standard (0.1 ppm or 0.25 mg/cu m).

The time to reach completion using a solution of pH 4.5 and GT concentration of 11.9×10^{-3} M, but varying the acrolein concentrations, was tested. Under these conditions, completion of the reaction was observed in 3 minutes over the acrolein concentration range of 0.524×10^{-5} M to 10.5×10^{-5} M.

It was also established that a graph of absorbance versus acrolein concentration was linear over this range.

The rate was studied as a function of pH. Acrolein and GT concentrations were 5.25×10^{-5} M and 11.6×10^{-3} M, respectively. The pH range tested was 2.21 to 6.38 using a citric acid/sodium monohydrogen phosphate buffer solution. Results of these tests indicated that the derivative was formed more quickly and in higher yield at low pH. For instance, the following absorbance readings were observed:

Table S21-2

pH	Time After Adding Acrolein	Absorbance
3.64	1 min	1.148
	10 min	1.160
	18 min	1.145
6.38	1.5 min	0.065
	10 min	0.130
	15 min	0.130

A pH of 4.5 was chosen based on the results of this study and the information contained in the studies of Conant and Bartlett (Reference 5). Conant and Bartlett studied the chemistry of semicarbazone formation with a number of carbonyl compounds to elucidate the factors which influence the reaction, and postulated that these principles are applicable to similar reactions. Our studies supported this view. Both the reaction rate and equilibrium position of the mixture are functions of the solution pH. Low pH increases the velocity of the forward reaction (derivative formation). This is desirable for collection of acrolein from air samples by use of a midget bubbler containing the reaction medium. High acidity also promotes hydrolysis, however, considerable hydrolysis will occur before the concentration of the derivative is measured, i.e., during transportation of the samples.

During the above tests, it was noticed in some cases that a decreased absorbance of the lower pH samples occurred after a period of time. Thus, stability tests were undertaken.

Solutions containing GT at a concentration of 11.6×10^{-3} M, and pH of 4.5, were spiked with acrolein and left on the laboratory bench for various periods of time. Significant losses in absorbance were found for long storage periods.

It was assumed at this time that hydrolysis of the derivative might be taking place, so a second set of samples was prepared, and the pH was adjusted to 6.5 after 1 hour. These samples showed a similar loss.

Another test was done in which ethanol was added to the samples. It was speculated that loss of acrolein from solution was occuring, and ethanol was added in an attempt to increase the acrolein solubility in the reaction medium. Again, significant losses were evident in less than 20 hours.

Solutions protected from light also gave lower absorbance readings after standing.

Next, the pure GT-acrolein derivative was prepared. Standards were made in distilled water and in solutions buffered at pH 4.65. Again, losses were noted when the samples were measured over a period of time. This test was undertaken to evaluate whether the excess GT was causing the decay, perhaps by reaction at the double bond of the derivative.

Table S21-3 summarizes the storage stability tests and the results.

It was obvious from these results that the use of this method would be unsatisfactory if samples were not analyzed immediately after collection.

In an effort to determine the mode of decay of the GT-acrolein derivative, a storage stability test similar to that described above was carried out using acetaldehyde, a carbonyl compound which does not have a double bond. It was found that no loss of this material occurred after 23.5 hours of storage.

One other method of stabilizing the acrolein derivative was attempted. This technique was utilization of the synergistic effect of hydroquinone, copper, and water to stabilize acrolein (Reference 6). While this method was intended to stabilize acrolein in manufacturing or plant transportation, it was hoped it would stabilize the derivative in the collection medium. Samples were prepared containing various combinations of hydroquinone, copper, and acrolein. These samples were stored at ambient laboratory light and temperature conditions for 24 hours before analysis. Standards were prepared the same day as analysis. Analyses were performed by sampled DC polarography.

The half-wave potential of the acrolein derivative at pH of 4.5 was -0.96 volts versus a saturated calomel electrode (SCE). All samples analyzed 24 hours after preparation exhibited a distinctive double wave. The half-wave potentials of these waves were -0.99 volts and -1.08 volts versus SCE. In addition, the total diffusion current for the stored samples was approximately one-half of that of samples analyzed immediately for those samples not containing copper. The sample containing copper did not show an appreciable decrease in total current, however,

Table S21-3

Stability Tests of GT-Acrolein Derivative

Solution Composition		pH	Time After Adding Acrolein	Absorbance
In Water				
Acrolein	GT			
9.0×10^{-6} M	10.4×10^{-3} M	4.4	0	0.180
			18 hr	0.090
			70 hr	0.038
9.0×10^{-6} M	10.4×10^{-3} M	6.5	1 hr*	0.175
			19 hr	0.090
			70 hr	0
5.4×10^{-5} M	10.4×10^{-3} M	4.4	0	Not measured
			16 hr	0.656
			69 hr	0.183
5.4×10^{-5} M	10.4×10^{-3} M	6.5	1 hr*	0.965
			16 hr	0.624
			69 hr	0.185
In Ethanol/Water				
5.6×10^{-5} M	10.4×10^{-3} M		1 hr	1.105
			18 hr	0.885
5.6×10^{-5} M	10.4×10^{-3} M		18 hr**	0.884
GT-Acrolein Derivative in Buffered Solution				
6.7×10^{-5} M (derivative)		4.65	0	1.645
			42 hr	1.060
4.9×10^{-5} M (derivative)		4.65	0	1.068
			43 hr	0.620
GT-Acrolein Derivative in Distilled Water				
6.7×10^{-5} M (derivative)			0	1.758
			47 hr	1.060

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* Sample prepared at solution pH of 4.4. Sodium hydroxide solution added after one hour to adjust pH to 6.5.

** Sample protected from light.

double wave was also evident. While the hydroquinone-copper stabilization method showed promise based on the 24-hour time study, it was decided to investigate other methods which would eliminate the problem of double polarographic waves.

Method Using Hydroxylamine Derivative

The second method tested was to react acrolein with hydroxylamine (Reference 7,8), another reagent known to react with aldehydes. Development of this method for the collection and analysis of acrolein was based on a sample size of 48 liters, collected at 0.2 liter/minute. Collected samples of 5.5, 11.0, and 22.0 micrograms represent 0.5X, 1X, and 2X the OSHA standard, respectively.

Hydroxylamine reacts with acrolein to form the oxime as shown in equation 2.

$$NH_2OH + CH_2{=}CH{-}CHO \rightleftarrows NOH{=}CH{-}CH{=}CH_2 + H_2O \qquad (2)$$

The pH of the collection medium affects both the diffusion current and the half-wave potential of the oxime. As the pH of the solution increases from 2 to 5.5, the diffusion current decreases 67%, and the half-wave potential decreases from -0.74 to -0.99 volts versus a SCE. It is reported that the maximum rate of oxime formation is at pH 5 and the maximum rate of hydrolysis at pH 2 (Reference 8). Considering the above information, it was decided to collect acrolein in a midget bubbler charged with 10 mL of a hydroxylamine solution at pH 5, then adjust the pH to 3.5 immediately before analysis.

The hydroxylamine concentration selected for the collection medium was 2×10^{-3} M which represents a 100-fold molar excess of the amount of acrolein to be collected at 1X the OSHA standard. The collection medium was adjusted to pH 5 with 0.1 M NaOH. Five milliliters of a pH 3.5 formic acid-sodium formate buffer was added before analysis and the analysis performed within 30 minutes. The acrolein oxime was sufficiently stable at this pH for up to a 30-minute wait prior to analysis. This buffer contained 0.1 M formic acid and 0.1 M sodium formate. This combination of pH 5 collection and pH adjustment for analysis allows for the formation of the oxime at its optimum pH and measurement at a pH where diffusion current will be greater. It was felt that adjusting the pH lower than 3.5 for analysis might result in loss of oxime by hydrolysis before analysis. Sample analysis was performed using a PAR 174 polarographic analyzer in the differential pulse mode. Conditions for analysis were a drop time of 1 second and a voltage scan rate of 5 mV/sec scanning from -0.6 volts to -1.2 volts.

A preliminary time study was conducted with spiked samples to determine if further investigation of this method was warranted. Three samples were prepared by spiking 14.26 micrograms of acrolein into 10 mL hydroxylamine solution. Analysis was performed after 3 days of storage at ambient laboratory light and temperature conditions. The results are in Table S21-4.

Table S21-4

Three-Day Time Study

Micrograms Spiked	Micrograms Found
14.26	14.76
14.26	14.64
14.26	14.88

The results of the above study indicate that the acrolein oxime is sufficiently stable for 3 days after formation.

Analytical Method Using Hydroxylamine

Spiked samples were prepared at 0.5X, 1X, and 2X the OSHA standard by spiking known amounts of acrolein into 10 mL of hydroxylamine. The pH was adjusted, and the samples were analyzed as previously described. The results of the analytical method recoveries are presented in Table S21-5.

Table S21-5

Acrolein Analytical Method Recovery (A.M.R.) Test

Level:	0.5X			1X			2X	
μg taken	μg found	A.M.R.	μg taken	μg found	A.M.R.	μg taken	μg found	A.M.R.
5.53	5.78	1.045	11.07	11.72	1.059	22.14	21.64	0.977
5.53	5.90	1.067	11.07	11.82	1.068	22.14	22.76	1.028
5.53	5.84	1.056	11.07	11.65	1.052	22.14	22.35	1.010
5.53	5.81	1.051	11.07	11.42	1.032	22.14	21.27	0.961
5.53	5.59	1.011	11.07	11.32	1.023	22.14	22.76	1.028
5.53	5.75	1.040	11.07	11.52	1.041	22.14	21.57	0.974
n		6			6			6
mean		1.045			1.046			0.996
std dev		0.019			0.017			0.029
CV		0.018			0.016			0.029

The analytical method was found to be satisfactory. The minimum detectable limit of the method was found to be 1.1 microgram/15 mL (5% of the 2X OSHA standard).

Generated Test Atmospheres

Test atmospheres of acrolein were generated by delivering an aqueous solution of acrolein of known concentration at a known flow rate into an all-glass system and diluting with a known volume of air. The section of the dilution system where acrolein in water was introduced was heated to vaporize the water and acrolein. Samples were collected using a midget bubbler containing 10 mL of hydroxylamine. Two sets of samples were collected from acrolein test atmospheres of 0.5X the OSHA standard using the hydroxylamine collection medium. Sampling rate for these tests was approximately 1 liter/minute. The results are presented in Table S21-6.

Polarograms of samples collected from the test atmosphere exhibited a double wave while standards prepared by spiking did not. The additional polarographic wave of collected samples corresponded to the half-wave potential of acrolein alone. It appeared from the results of analyses of these samples that acrolein was not completely derivatized in the bubbler.

Table S21-6

0.5X OSHA Standard Generation

Set 1

Found			Taken	
µg	Liters	mg/cu m	mg/cu m	Recovery
3.27	45.6	0.0717	0.1030	
3.40	47.8	0.0711	0.1030	
3.86	51.3	0.0752	0.1030	
3.27	46.9	0.0697	0.1030	
3.01	47.6	0.0632	0.1030	
	n = 5			
	mean	0.0702		0.682
	std dev	0.0044		
	CV_2	0.063		

Set 2

3.27	45.9	0.0712	0.1160	
3.61	48.2	0.0749	0.1160	
3.56	51.7	0.0689	0.1160	
3.47	50.0	0.0694	0.1160	
3.42	47.2	0.0725	0.1160	
3.42	47.9	0.0714	0.1160	
	n = 6			
	mean	0.0714		0.616
	std dev	0.0022		
	CV_2	0.031		

An increase in hydroxylamine concentration should increase the forward reaction rate. The hydroxylamine concentration was increased to 9.8 x 10^{-3} M. The results of analyzed samples are presented in Table S21-7.

Table S21-7

---------------Found---------------			Taken	
µg	Liters	mg/cu m	mg/cu m	Recovery
3.78	50.7	0.0746	0.1160	
4.06	47.4	0.0857	0.1160	
3.81	47.7	0.0799	0.1160	
3.56	45.4	0.0784	0.1160	
3.68	48.7	0.0756	0.1160	
3.56	47.4	0.0751	0.1160	
	n = 6			
	mean	0.0782		0.674
	std dev	0.0042		
	CV_2	0.054		

Increasing the concentration of hydroxylamine did not increase the apparent collection efficiency. In addition, hydroxylamine at these concentrations introduced significant background. It was concluded that the hydroxylamine concentration was sufficiently high at 2 x 10^{-3} M.

The solvent used for the acrolein generation solution in further generations was methanol. This change allowed the use of less heat to vaporize the solvent. It was thought that excess heat may have caused some acrolein loss in the generator, and the taken concentration was actually lower than calculated.

Test atmospheres were next generated at 2X the OSHA standard and samples taken at various flow rates. Sample flow rates of 0.2, 0.5, and 1.0 liter/min were used to determine their effects on collection efficiency. All samples were collected using two bubblers connected in series, and the amount of acrolein passing through a single bubbler was determined. All samples were collected from the same test atmosphere, but not for the same period of time. The results of analysis are in Table S21-8.

From these tests, it was clear that adequate collection efficiency could be achieved only at flow rates of 0.2 liter/minute or lower. However, at these low flow rates, the amount of acrolein collected at the 1X level would be so low that the precision of the analytical measurement would be unacceptable.

Conclusions

Experimental work indicates neither of the two derivatization techniques explored are satisfactory for the collection and analysis of acrolein. The collection efficiency of the hydroxylamine solution was unsatisfactory. The collection efficiency of a buffered Girard T reagent medium is not known. The Girard T reagent-acrolein derivative was found to be unstable.

Recommendations

It seems unlikely that a method for the collection and analysis of acrolein can be developed based on collection in a midget bubbler, with simultaneous derivatization by hydroxylamine to form the oxime.

It is recommended further experimental work be conducted to determine the collection efficiency of the buffered Girard T reagent collection medium. Should these tests prove successful, it is further recommended that a mechanism for stabilization of the derivative be investigated.

It is probable that stabilization of acrolein will be successful only if complexation or reaction of the double bond occurs.

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