Method number:	108
Matrix:	Air
Target concentration:	10 ppb (13 µg/m^3) and 1 ppm (1.3 mg/m^3)
OSHA PEL:	1 ppm (1.3 mg/m^3)
ACGIH TLV:	10 ppb (13 µg/m^3)
Procedure:	Samples are collected closed-face by drawing known volumes of air through sampling devices consisting of three-piece cassettes, each containing two sulfuric acid treated 37-mm glass fiber filters separated by the ring section. The filters are extracted with a buffered EDTA disodium solution. An aliquot of the extract is derivatized with a benzaldehyde solution to form benzalazine from any hydrazine in the samples. The benzalazine is quantitated by LC using a UV detector.
Recommended air volume and sampling rate:	240 L at 1.0 L/min
Reliable quantitation limit:	0.058 ppb (0.076 µg/m^3)
Standard error of estimate at the target concentration:	7.5% at 10 ppb Target Concentration 5.2% at 1 ppm Target Concentration
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: February 1997

Chemist: Carl J. Elskamp

Organic Methods Evaluation Branch
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1. General Discussion

1.1 Background

1.1.1 History

In 1980, an air sampling and analytical procedure to determine hydrazine was validated by the OSHA Analytical Laboratory. (Ref. 5.1) The method (OSHA Method 20) is based on a field procedure developed by the U.S. Air Force that involves collection of samples using sulfuric acid coated Gas Chrom R and colorimetric analysis using *p*—dimethylaminobenzaldehyde. (Ref. 5.2) Because colorimetric procedures are more susceptible to interferences, an LC analysis procedure was also developed by OSHA in Method 20 where benzalazine, the reaction product between hydrazine and benzaldehyde, is quantitated using a UV detector.

After Method 20 was completed, sulfuric acid treated Gas Chrom R adsorbent tubes became commercially available. Since that time, the OSHA SLTC (Salt Lake Technical Center) has received comments from other laboratories reporting low extraction efficiencies and sample recoveries when using the commercial tubes. It was decided that these concerns would be investigated. Also, because ACGIH lowered the TLV from 100 ppb to 10 ppb (Ref. 5.3) since Method 20 was validated and because OSHA may consider lowering the PEL from 1 ppm in the future, the methodology was evaluated at lower levels with test atmospheres. It was not possible for OSHA to generate hydrazine test atmospheres when Method 20 was validated. Since that time, a controlled test atmosphere generation system was constructed at the OSHA SLTC that can be used to safely generate atmospheres from toxic compounds such as hydrazine.

A 2.1-ppm atmosphere was generated and samples were collected using both commercial sulfuric acid treated Gas Chrom R sampling tubes and sampling tubes that were prepared in-house. Both samplers gave similar recoveries, but most of the hydrazine was found on the front glass wool plug of the commercial tubes. This indicated that as prepared samplers are stored for an extended period of time before use, some of the sulfuric acid apparently migrates to the glass wool plugs, turning the plug into an effective sampler for hydrazine. It is not known how old the commercial tubes were for this study, but they were probably several years old. It was felt that the commercial tubes would be suitable, as long as the glass wool plug was extracted and analyzed along with the treated Gas Chrom R. But further tests at ppb levels of hydrazine showed poor recoveries and poor sample extract stability from acid treated Gas Chrom R, especially for the commercial tubes. The poor recoveries and stability may be attributed to the possible presence of trace metals in the adsorbent, which was indicated by the yellow color of EDTA extracts of the acid treated Gas Chrom R. The EDTA extracts from the commercial tubes were deeper yellow than that from the in-house prepared tubes, suggesting the presence of more metals. It was also found that the commercially prepared tubes had a higher acid content than the in-house tubes, which may be important for recovery yields because the reaction between hydrazine and benzaldehyde is somewhat pH dependent. An alternate sampling device that would avoid the problems associated with acid treated Gas Chrom R was desirable. A promising candidate was a sampler consisting of sulfuric acid treated glass fiber filters that had been validated by the OSHA SLTC for a number of aromatic amines (Refs. 5.4-5.11).

Initial tests using sulfuric acid treated Gelman A/E filters at ppm levels of hydrazine showed collection efficiencies, recoveries, and extraction efficiencies to be essentially 100%. The recovery of hydrazine collected from test atmospheres is not quite as good at ppb levels. In an attempt to enhance recoveries, filters treated with either EDTA or Vitamin C alone or with sulfuric acid were tested with no improvement. The filters were also treated with different mineral acids, including hydrochloric, nitric and phosphoric acid, but again recoveries were no better than when just sulfuric acid was used. Gelman A/E filters were used in the methods for aromatic amines and may be suitable for hydrazine, but it was

found that the thicker A/B filters formed tighter seals in the filter cassettes and they also provided slightly better collection efficiencies. The A/B filters can also be used for aromatic amines with no other change in the methods.

Improvements were also made to the analytical procedure. It was found that the room temperature formation of benzalazine from hydrazine and benzaldehyde proceeded to completion in less than 30 minutes at about pH 3.5. Also, the use of EDTA disodium enhanced the stability of extracted samples, so an aqueous EDTA disodium solution buffered to pH 3.5 is used to extract the filter samples. Acetonitrile is now used instead of methyl alcohol as the solvent for benzaldehyde. The recommended air volume was 20 L in Method 20, but in order to obtain a lower reliable quantitation limit and to have a more convenient sampling time of 4 hours, 240 L is the new recommended air volume. The amount of benzalazine formed from 240-L samples at ppm levels was found to be somewhat insoluble in methyl alcohol, but was found to be much more soluble in acetonitrile.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

Hydrazine is carcinogenic in experimental animals and is a suspected human carcinogen. (Ref. 5.3) It is corrosive to the eyes, skin, and mucous membranes. The liver, kidney, and hematopoietic system are the main target organs following repeated exposures. (Ref. 5.12)

1.1.3 Workplace exposure

Hydrazine is chiefly used as a chemical intermediate in the production of agricultural chemicals, spandex fibers and antioxidants. It is also used as a rocket fuel, oxygen scavenger in boiler water treatment, polymerization catalyst, blowing agent, and scavenger for gases. (Ref. 5.3)

1.1.4 Physical properties (Ref. 5.13 unless otherwise denoted)

CAS number:	302-01-2
molecular weight:	32.06
boiling point:	113.5°C
melting point:	1.4°C
appearance:	colorless, oily, fuming liquid or white crystals
density:	1.1011 at 15°C
molecular formula:	H_4N_2
vapor pressure:	1.3 kPa at 20°C (Ref. 5.3)
flash point:	100°F (37.8°C) (open cup)
odor:	penetrating, resembling ammonia
lower explosive limit:	4.7% (Ref. 5.3)
synonyms:	Diamide; diamine; hydrazine, anhydrous (DOT); hydrazine, aqueous solution (DOT); hydrazine base; hydrazyna (Polish); RCRA waste number U133
structural formula:	H_2NNH_2

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppb and ppm are referenced to 25°C and 101.3 kPa (760 mmHg). Although benzalazine is the actual species analyzed, all masses presented are in terms of hydrazine.

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 10.6 pg. This is the amount of analyte that will give a response that is significantly different from the background response of a reagent blank. (Sections 4.1 and 4.2)

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 5.48 ng per sample (0.017 ppb or 0.023 $\mu g/m^3$). This is the amount of analyte spiked on the sampler that will give a response that is significantly different from the background response of a sampler blank. (Sections 4.1 and 4.3)

1.2.3 Reliable quantitation limit

The reliable quantitation limit is 18.3 ng per sample (0.058 ppb or 0.076 $\mu g/m^3$). This is the amount of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements. (Section 4.4)

1.2.4 Precision (analytical procedure)

The precisions of the analytical procedure, measured as the pooled relative standard deviation over concentration ranges equivalent to 0.5 to 2 times the target concentration, are 0.26% and 0.09% based on the 10-ppb and the 1-ppm target concentrations respectively. (Section 4.5)

1.2.5 Precision (overall procedure)

The precisions of the overall procedure at the 95% confidence level for the ambient temperature storage tests are ±14.8% and ±10.1% at 9.4 ppb and 1.06 ppm respectively. These include an additional 5% for sampling error. (Section 4.6)

1.2.6 Recovery

The recovery of hydrazine from samples used in a 19-day storage test remained above 78% at the 10-ppb target concentration when the samples were stored at ambient temperatures. The recovery of hydrazine from samples used in a 20-day storage test remained above 96% at the 1-ppm target concentration when the samples were stored at ambient temperatures. (Section 4.7)

1.2.7 Reproducibility

Six samples at each target concentration that were collected from controlled test atmospheres, along with a draft copy of this procedure, were submitted to an SLTC service branch for analysis. The samples were analyzed after 63 and 58 days of storage at 0°C for the 10-ppb and 1-ppm target concentrations respectively. One of the 10-ppb target concentration samples was an outlier, while none of the remaining sample results deviated from its theoretical value by more than the precisions reported in Section 1.2.5. (Section 4.8)

2. Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump calibrated, with a sampling device attached, to within ±5% at the recommended flow rate.

2.1.2 Samples are collected closed-face using a sampling device consisting of two sulfuric acid treated 37-mm Gelman Sciences type A/B glass fiber extra thick filters (part no. 66208) contained in a three-piece SAN (styrene acrylonitrile) plastic cassette (Gelman part no. 4339 or Millipore Corp., Bedford, MA, part no. M000037A0). The filters are prepared by soaking each filter with 1.0 mL of 0.26 N sulfuric acid. The 0.26 N sulfuric acid can be prepared by diluting 1.5 mL of 36 N sulfuric acid to 200 mL with either methyl alcohol or deionized water. The filters are dried in an exhaust hood when a methanolic solution is used and in an oven at 100°C when an aqueous solution is used and then assembled into three-piece 37-mm cassettes without support pads. The front filter is separated from the back filter by the ring section. The cassettes are sealed with shrink bands and the ends are plugged with plastic plugs.

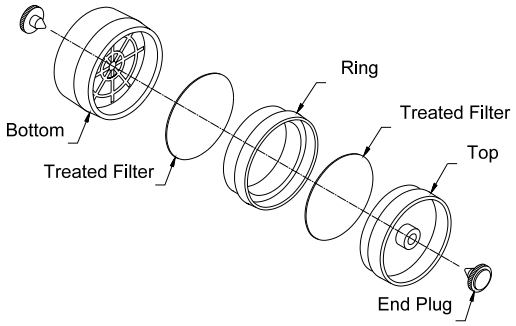

Figure 1

2.2 Reagents

None required

2.3 Technique

2.3.1 Remove the plastic end plugs from the sampling device immediately before sampling. Samples are collected closed-face.

2.3.2 Attach the sampling device to the sampling pump with flexible tubing and place the device in the employee's breathing zone. Position the sampler so it does not impede work performance or safety.

2.3.3 Do not pass the sampled air through any hose or tubing before it enters the sampling device.

2.3.4 Immediately after sampling, seal the sampling device with plastic end plugs and seal and identify with a Form OSHA-21 seal.

2.3.5 Submit at least one blank with each sample set. Blanks should be handled in the same manner as samples, except no air is drawn through them.

2.3.6 Record sample volumes (in liters of air) for each sample. Also list any compounds considered potential interferences that could be present in the sampling area.

2.3.7 If any bulk samples are submitted for analysis, ship them in separate containers from the air samples.

2.3.8 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at reduced temperature.

2.4 Sampler capacity

Sampler capacity is determined by measuring how much air can be sampled before breakthrough of analyte through the sampler occurs, i.e., the sampler capacity is exceeded. Breakthrough is considered to occur when the effluent from the sampler contains a concentration of analyte that is 5% of the upstream concentration (5% breakthrough). Tests for breakthrough were performed by simultaneously sampling at 1 L/min from a hydrazine atmosphere (81.5% RH, 23.6°C) at 2.1 ppm using four samplers. The sampler flows were momentarily interrupted and the back filters were removed and replaced with fresh filters every hour after sampling began over a period of 8 hours. The back filters were analyzed to determine the hydrazine concentration in the effluents. At no time during the 8-hour tests did the effluent concentrations exceed 5% of the upstream concentration for any of the four samplers. The filters are coated with an amount of sulfuric acid that could theoretically collect about 4.5 mg of hydrazine. For a 240-L air sample, this would be equal to 14.3 ppm (18.8 mg/m^3).

2.5 Extraction efficiency

2.5.1 The average extraction efficiencies over the range of 0.5 to 2 times the target concentrations are 98.7% and 98.9% based on the 10-ppb and 1-ppm levels respectively. (Section 4.9.1)

2.5.2 The extraction efficiency at 0.05, 0.1, and 0.2 times the target concentration was found to be 97.7%, 97.5%, and 96.3% respectively based on the 10-ppb level and 98.2%, 98.0%, and 98.6% respectively based on the 1-ppm level. (Section 4.9.1)

2.5.3 Both extracted and extracted/derivatized samples at each target concentration remain stable for at least 24 h. (Section 4.9.2)

2.6 Recommended air volume and sampling rate

2.6.1 For long-term samples, sample 240 L of air at 1 L/min (4-h samples).

2.6.2 For short-term samples, sample 15 L of air at 1 L/min (15-min samples).

2.6.3 When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit is 0.93 ppb (1.22 $\mu g/m^3$) when 15 L of air is sampled.

2.7 Interferences (sampling)

2.7.1 It is not known if any compounds will severely interfere with the collection of hydrazine on sulfuric acid treated filters. In general, any compound in the sampled air that would react with sulfuric acid to decrease the amount on the filter will decrease the breakthrough volume. Also, any compound that will react with hydrazine or hydrazine sulfate is a potential interference.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precautions (sampling)

2.8.1 Attach the sampling equipment to the employee so that it will not interfere with work performance or safety.

2.8.2 Follow all safety procedures that apply to the work area being sampled.

3. Analytical Procedure

3.1 Apparatus

3.1.1 An LC system equipped with an ultraviolet detector. A Hewlett-Packard 1050 Series LC consisting of a pumping system, a programmable variable wavelength detector and an autosampler was used in this evaluation.

3.1.2 An LC column capable of separating the analyte of interest from any interferences. A 12.5-cm × 4-mm i.d. LiChrospher 100 RP-18 column (Hewlett-Packard Company, part no. 79925OD-564) was used in this evaluation.

3.1.3 An electronic integrator or some other suitable means of measuring peak areas or heights. A Waters Millennium Networking Computer System was used in this evaluation.

3.1.4 Glass vials with Teflon®-lined caps. Kimble Glass Co. 7-mL disposable scintillation vials (part no. 74502-7) and Thomas Scientific caps (cat. no. 2390-B16) were used in the preparation of standards and extraction of sample filters. National Scientific Co. 2-mL Target DP™ vials and caps (part no. C4000-1 and C4000-54Y respectively) were used in the derivatization of standards and filter extracts.

3.1.5 Hand held dispensers (repeating pipettors) capable of delivering 0.5, 1.0 and 5.0 mL for preparing and transferring standards and sample extracts and for dispensing the derivatizing solution. If dispensers are not available, volumetric pipettes may be used instead.

3.1.6 A test tube rotator to mix the samples during the extraction step.

3.1.7 A laboratory centrifuge.

3.2 Reagents

3.2.1 Hydrazine or hydrazine solution, reagent grade. Aldrich Chemical (Milwaukee, WI) Lot 21131EN anhydrous hydrazine was used in this evaluation. Hydrazine is a highly toxic sensitizer, mutagen, and cancer suspect agent that is readily absorbed through skin. It is also a corrosive and combustible liquid and a strong reducing agent that should be stored under nitrogen.

Standards may alternatively be prepared from reagent grade benzalazine or from a reagent grade hydrazine salt, such as hydrazine dihydrochloride or hydrazine sulfate.

3.2.2 Acetonitrile, methanol, and water, LC grade. The acetonitrile and methanol used in this evaluation were "Optima" brand from Fisher Chemical (Fair Lawn, NJ) and the water was from a Millipore Milli-Q water purification system.

3.2.3 Benzaldehyde, reagent grade. Aldrich Lot 03628KN was used in this evaluation. Benzaldehyde is an irritant, mutagen, sensitizer, and cancer suspect agent. It is air and light sensitive and should be store under nitrogen.

3.2.4 Sodium phosphate, monobasic monohydrate ($NaH_2PO_4 \bullet H_2O$), reagent grade. Fisher Lot 704979 was used in this evaluation.

3.2.5 EDTA disodium, from ethylenediaminetetraacetic acid, disodium salt dihydrate, reagent grade. Aldrich Lot 14428LZ was used in this evaluation.

3.2.6 Phosphoric acid, reagent grade.

3.2.7 Extraction solution, consisting of an aqueous solution of 0.1 M $NaH_2PO_4 \cdot H_2O$/0.05 M EDTA disodium adjusted to pH 3.5 with phosphoric acid.

3.2.8 Derivatizing solution, prepared by diluting 1.0 mL of benzaldehyde to 100 mL with acetonitrile. The derivatizing solution should be prepared fresh daily.

3.3 Standard preparation

3.3.1 Prepare concentrated stock solutions by accurately diluting a known amount of hydrazine with methanol. Stock solutions are stable for at least 3 days when refrigerated. Standards can alternatively and more conveniently be prepared from hydrazine dihydrochloride, hydrazine sulfate or benzalazine. Stock standards from hydrazine salts should be prepared in water, while standards from benzalazine should be prepared in acetonitrile. If standards are preprared from one of the salts or benzalazine, the appropriate conversion factor to determine the equivalent mass of hydrazine must be used. For example, if hydrazine sulfate (MW = 130.12) is used to make standards, the mass of hydrazine sulfate weighed out must be multiplied by 0.2464 (32.06 ÷ 130.12) to obtain the equivalent mass of hydrazine.

3.3.2 Prepare analytical standards by injecting microliter amounts of stock standards into 7-mL vials containing 5.0 mL of extraction solution delivered from the same dispenser or pipet used to extract samples.

3.3.3 Derivatize the analytical standards by transferring 1.0 mL of the standards to separate autosampler vials and adding 0.5 mL of derivatizing solution to each vial. Cap each vial and shake it for a few seconds to obtain thorough mixing. Allow the vials to sit at room temperature for at least 30 min before analysis. Analyze the derivatized standards by LC.

3.3.4 Bracket sample concentrations with analytical standard concentrations. If samples fall outside of the concentration range of prepared standards, prepare and analyze additional standards at the appropriate concentrations to ascertain the linearity of response. Theoretically, there is enough benzaldehyde added to the vials to prepare standards as high as 2.5 ppm for 240-L air samples (789 µg/sample). Alternatively, if sample concentrations are higher than the highest standard, the extracts can be diluted with extraction solution, and 1.0 mL aliquots of the diluted extracts can be derivatized and analyzed.

3.4 Sample preparation

3.4.1 Transfer front and back filters to individual 7-mL vials.

3.4.2 Add 5.0 mL of extraction solution to each vial using the same dispenser or pipet as used for preparation of standards.

3.4.3 Cap the vials and mix them on a rotator for 30 min.

3.4.4 Centrifuge the sample vials for 10 min at 2000 rpm.

3.4.5 Derivatize the samples by transferring 1.0 mL of the centrifuged extracts to separate autosampler vials and adding 0.5 mL of derivatizing solution to each vial. Cap each vial and shake them for a few seconds to obtain thorough mixing. Allow the vials to sit at room temperature for at least 30 min before analysis. Analyze the derivatized samples by LC. As a precautionary step, the sample extracts should be derivatized as soon as possible after they are extracted and centrifuged.

3.5 Analysis

3.5.1 LC conditions

mobile phase:	67/33, acetonitrile/water
flow rate:	1.0 mL/min
UV detector wavelength:	300 nm
detector range:	2 AUFS for 1-ppm target concentration 0.02 AUFS for 10-ppb target concentration
injection volume:	4.5 µL
column:	12.5-cm × 4-mm i.d. LiChrospher 100 RP-18
retention time:	5.8 min

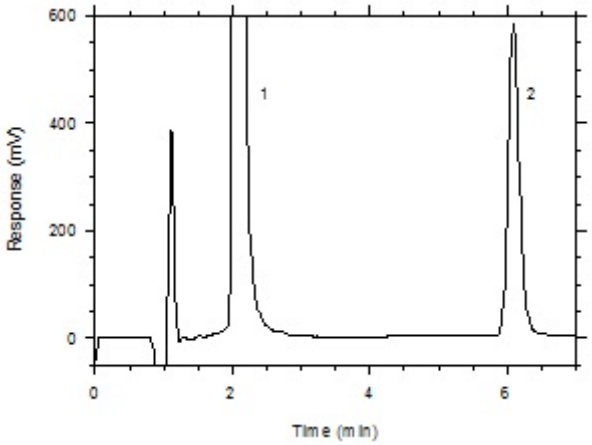

Figure 2 Figure 3.5.1.1. Chromatogram of a 10-ppb target concentration (3187 ng/sample) standard obtained at 0.02 AUFS. Key: (1) excess benzaldehyde, (2) benzalazine (as hydrazine).

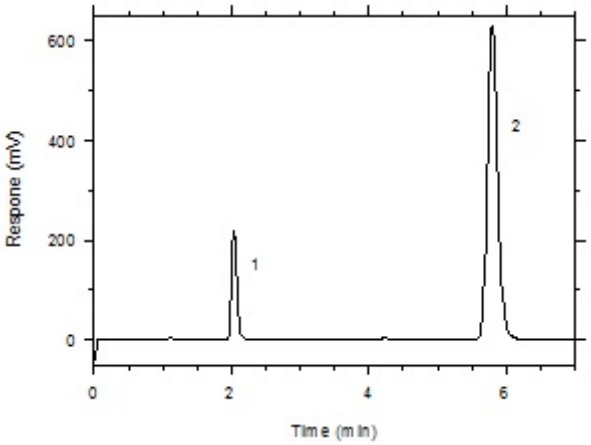

Figure 3 Figure 3.5.1.2. Chromatogram of a 1-ppm target concentration (318.7 µg/sample) standard obtained at 2 AUFS. Key: (1) excess benzaldehyde, (2) benzalazine (as hydrazine).

3.5.2 Peak areas or heights are measured by an integrator or other suitable means.

3.5.3 An external standard (ESTD) calibration method is used. Calibration curves are prepared by plotting the amount of analyte per sample versus peak heights or area counts of the standards. Sample concentrations must be bracketed by standards.

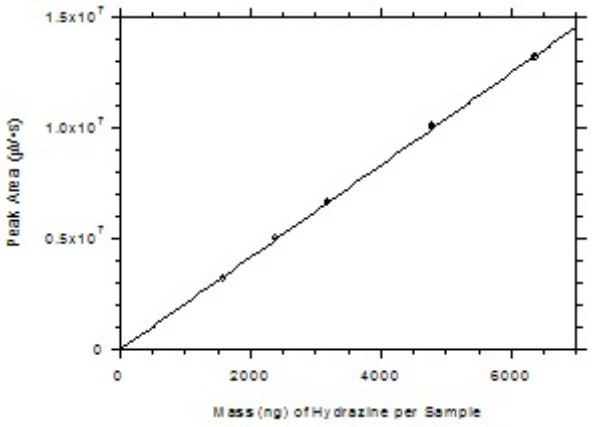

Figure 4 Figure 3.5.3.1. Calibration curve constructed from the data in Table 4.5.1. The equation of the line is Y = 2087X - 49650.

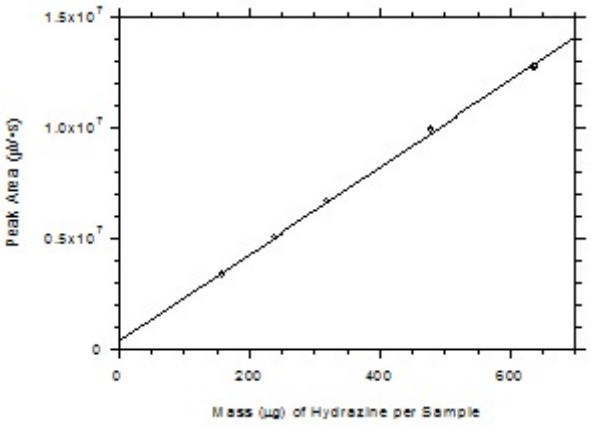

Figure 5 Figure 3.5.3.2. Calibration curve constructed from the data in Table 4.5.2. The equation of the line is Y = 19700X + 314500.

3.6 Interferences (analytical)

3.6.1 Any compound that produces a response on a UV detector at 300 nm and has the same general retention time of benzalazine is a potential interference. Possible interferences should be reported to the laboratory with submitted samples by the industrial hygienist. These interferences should be considered before samples are extracted.

3.6.2 LC parameters may be changed to possibly circumvent interferences.

3.6.3 When necessary, the identity or purity of an analyte peak may be confirmed with additional analytical data, such as wavelength ratioing. As an aid in choosing appropriate wavelengths to ratio, the UV spectrum of benzalazine is given in Section 4.10.

3.7 Calculations

The hydrazine concentration for samples is obtained from the calibration curve in terms of micrograms of hydrazine per sample. The back filter of each sampler is analyzed primarily to determine if there was any breakthrough from the front filter during sampling. If a significant amount of analyte is found on the back filter, this fact should be reported with sample results. If any analyte is found on the back filter, it is added to the amount found on the front filter. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formula.

mg/m^3 = (µg of hydrazine per sample)/[(L of air sampled)(extraction efficiency)]

ppm = [$(mg/m^3)(24.46)$]/32.06 = $(mg/m^3)(0.7629)$

3.8 Safety precautions (analytical)

3.8.1 Adhere to the rules set down in your Chemical Hygiene Plan.

3.8.2 Avoid skin contact and inhalation of all chemicals.

3.8.3 Wear safety glasses and a lab coat at all times while in the lab area.

4. Backup Data

4.1 Determination of detection limits

Detection limits (DL), in general, are defined as the amount (or concentration) of analyte that gives a response (Y_{DL}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DL} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{BR} in chromatographic methods is typically inconvenient and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of analytical standards or samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for DL:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

Y_{obs} = observed response
Y_{est} = estimated response from regression curve
n = total no. of data points
k = 2 for a linear regression curve

$$Y_{DL} = A(DL) + Y_{BR}$$

At point Y_{DL} on the regression curve
A = analytical sensitivity (slope)

therefore

$$DL = \frac{(Y_{DL} - Y_{BR})}{A}$$

Substituting 3(SEE) + Y_{BR} for Y_{DL} gives

$$DL = \frac{3(SEE)}{A}$$

4.2 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as the mass of analyte introduced into the chromatographic column. Ten analytical standards were prepared in equal descending increments with the highest standard containing 31.88 ng of hydrazine per sample. This standard produces a peak approximately 10 times the baseline noise of a reagent blank. Standards, plus a reagent blank, were analyzed and the data obtained were used to determine the required parameters (A and SEE) for the calculation of the DLAP. Values of 2222 and 7881 were obtained for A and SEE respectively. The DLAP was calculated to be 10.6 pg.

Table 4.2
DLAP for Hydrazine

concentration (ng/sample)	mass on column (pg)	peak area (μV•s)
0.000	0.00	0
3.188	1.913	8809
6.376	3.826	23226
9.564	5.738	36406
12.75	7.651	27240
15.94	9.564	26618
19.13	11.48	32833
22.32	13.39	49718
25.50	15.30	35622
28.69	17.22	49097
31.88	19.13	47417

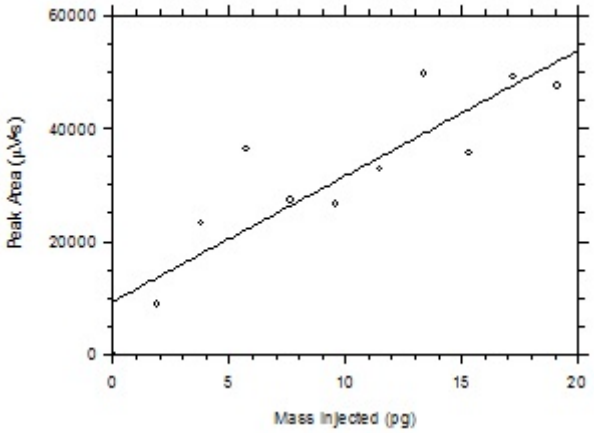

Figure 4.2. Plot of the data from Table 4.2 to determine the DLAP of 10.6 pg. The equation of the line is Y = 2222X + 9379.

4.3 Detection limit of the overall procedure (DLOP)

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of hydrazine such that the highest sampler loading was 31.88 ng/sample. This is the amount, when spiked on a sampler, that would produce a peak approximately 10 times the baseline noise for a sample blank. These spiked samplers, plus a sample blank, were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (A and SEE) for the calculation of the DLOP. Values of 1553 and 2839 were obtained for A and SEE respectively. The DLOP was calculated to be 5.48 ng/sample (0.017 ppb or 0.023 μg/m^3).

Table 4.3
Detection Limit of the Overall Procedure

mass (ng) per sample	peak area (µV•s)
0.000	0
3.188	9000
6.376	11917
9.564	17427
12.75	19696
15.94	32303
19.13	30798
22.32	34371
25.50	37687
28.69	49149
31.88	52342

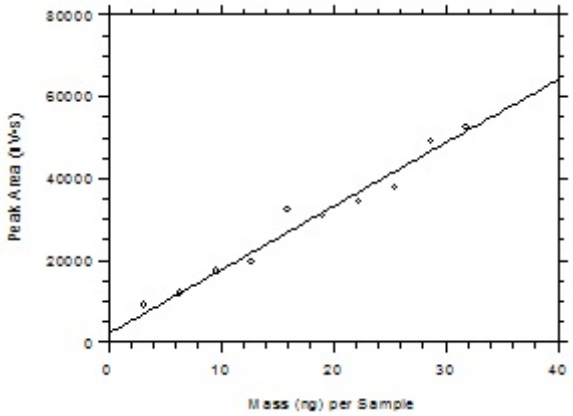

Figure 4.3. Plot of data from Table 4.3 to determine the DLOP of 5.48 ng/sample (0.017 ppb or 0.023 µg/m^3). The equation of the line is Y = 1553X + 2035.

4.4 Reliable quantitation limit (RQL)

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line data obtained for the calculation of the DLOP (Section 4.3). The RQL is defined as the amount of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

therefore

$$RQL = \frac{10(SEE)}{A}$$

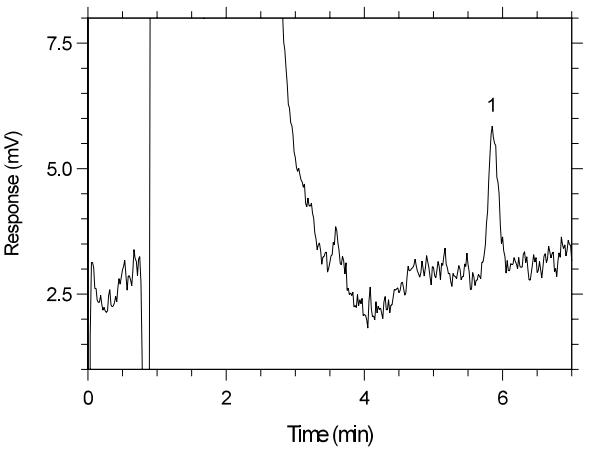

Figure 4.4. Chromatogram of the RQL. Key: (1) Benzalazine (as hydrazine).

The RQL was calculated to be 18.3 ng/sample (0.058 ppb or 0.076 µg/m^3). The recovery at this level is 90.2%.

4.5 Precision (analytical method)

The precisions of the analytical procedure are defined as the pooled relative standard deviations (RSD_P). Relative standard deviations were determined from six replicate injections of standards at 0.5, 0.75, 1, 1.5, and 2 times the target concentrations. After assuring that the RSDs satisfy the Cochran test for homogeneity at the 95% confidence level, the RSD_Ps were calculated to be 0.26% and 0.09% based on the 10-ppb and 1-ppm target concentrations respectively.

Table 4.5.1
Instrument Response Based on a 10-ppb Target Concentration

× target concn (ng/sample)	0.5× 1594	0.75× 2390	1.0× 3187	1.5× 4781	2.0× 6374
peak areas (µV•s)	3187300	5022900	6648300	10115000	13192000
	3176400	5002500	6601100	10032000	13161000
	3164800	5006200	6615000	10035000	13144000
	3175300	5001200	6595100	10043000	13184000
	3173000	4991800	6620900	10017000	13167000
	3176900	4996400	6627700	10026000	13130000
mean	3175600	5003500	6618000	10045000	13163000
SD	7248.6	10745	19181	35545	23461
RSD (%)	0.228	0.215	0.290	0.354	0.178

The Cochran test for homogeneity:

$$g = \frac{\text{largest } RSD^2}{RSD_{0.5\times}^2 + RSD_{0.75\times}^2 + RSD_{1\times}^2 + RSD_{1.5\times}^2 + RSD_{2\times}^2} = 0.369$$

The critical value of the *g* statistic at the 95% confidence level for five variances, each associated with six observations, is 0.5065. Because the *g* statistic does not exceed this value, the RSDs can be considered equal and they can be pooled (RSD_P) to give an estimated RSD for the concentration range studied.

$$RSD_P = \sqrt{\frac{5(RSD_{0.5\times}^2+RSD_{0.75\times}^2+RSD_{1\times}^2+RSD_{1.5\times}^2+RSD_{2\times}^2)}{5+5+5+5+5}} = 0.26\%$$

Table 4.5.2
Instrument Response Based on a 1-ppm Target Concentration

× target concn (µg/sample)	0.5× 159.4	0.75× 239.0	1.0× 318.7	1.5× 478.1	2.0× 637.4
peak areas (µV•s)	3338300	5030400	6668100	9869800	12721000
	3331000	5035000	6672700	9877700	12741000
	3334800	5036400	6674500	9877900	12744000
	3336100	5039600	6682700	9878900	12745000
	3336200	5040700	6684100	9879000	12746000
	3336800	5046400	6685400	9890700	12752000
mean	3335500	5038100	6677900	9879000	12742000
SD	2494.5	5471.5	7104.5	6699.9	10672
RSD (%)	0.075	0.109	0.106	0.068	0.084

The Cochran test for homogeneity:

$$g = \frac{\text{largest RSD}^2}{RSD_{0.5\times}^2 + RSD_{0.75\times}^2 + RSD_{1\times}^2 + RSD_{1.5\times}^2 + RSD_{2\times}^2} = 0.294$$

The critical value of the *g* statistic at the 95% confidence level for five variances, each associated with six observations, is 0.5065. Because the *g* statistic does not exceed this value, the RSDs can be considered equal and they can be pooled (RSD_P) to give an estimated RSD for the concentration range studied.

$$RSD_P = \sqrt{\frac{5(RSD_{0.5\times}^2+RSD_{0.75\times}^2+RSD_{1\times}^2+RSD_{1.5\times}^2+RSD_{2\times}^2)}{5+5+5+5+5}} = 0.090\%$$

4.6 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data in Section 4.7. The determination of the standard error of estimate (SEE_R) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE_R is similar to the standard deviation, except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

$$SEE_R = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

n = total no. of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed % recovery at a given time
Y_{est} = estimated % recovery from the regression line at the same given time

An additional 5% for pump error (SP) is added to the SEE_R by the addition of variances to obtain the total standard error of estimate.

$$SEE = \sqrt{(SEE_R)^2 + (SP)^2}$$

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate (with pump error included) by 1.96 (the *z* statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression lines in the storage graphs, as shown in Figures 4.7.1.1, 4.7.1.2, 4.7.2.1 and 4.7.2.2. The precisions of the overall procedure of ±14.8% and ±10.1% were obtained from Figures 4.7.1.2 and 4.7.2.2 for 10-ppb and 1-ppm target concentrations respectively.

4.7 Storage test

Storage samples were prepared by sampling at 1 L/min from two different controlled test atmospheres, one at 9.40 ppb and the other at 1.06 ppm. Both atmospheres were at approximately 80% RH and at room temperatures ranging from 22-26°C. Six samples for each level were analyzed immediately after generation, fifteen were stored in a refrigerator at 0°C, and fifteen were stored in a closed drawer at ambient temperatures of 20-25°C. At approximately three-day intervals, three samples were selected from each of the two storage sets for each level and analyzed.

Table 4.7.1
Storage Test at 9.40 ppb

time (days)	refrigerated storage recovery (%)			ambient storage recovery (%)		
0	90.7	72.4	84.5	90.7	72.4	84.5
0	90.9	94.9	85.7	90.9	94.9	85.7
3	82.0	90.1	81.4	83.8	87.0	86.6
6	90.0	92.6	86.8	78.9	90.0	86.9
11	92.8	89.3	83.6	75.8	77.8	80.3
14	91.3	94.6	82.6	83.3	79.6	75.2
19	86.8	98.2	89.4	77.9	74.5	88.7

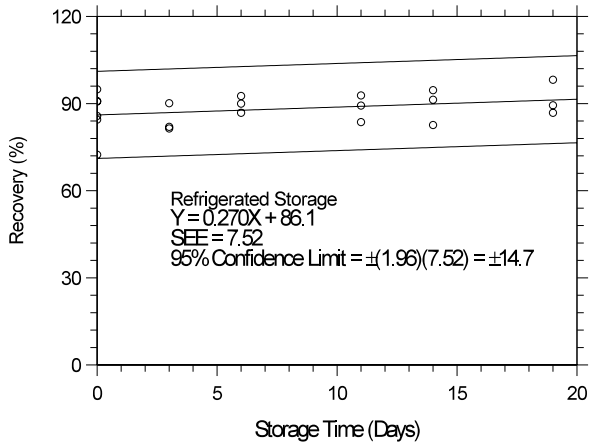

Figure 4.7.1.1. Refrigerated storage test at 9.40 ppb.

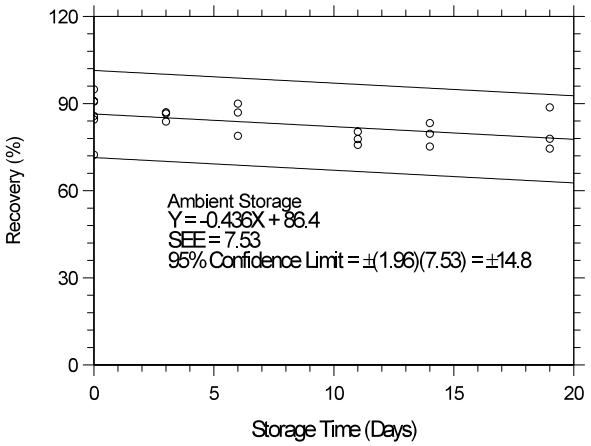

Figure 4.7.1.2. Ambient storage test at 9.40 ppb.

Table 4.7.2
Storage Test at 1.06 ppm

time (days)	refrigerated storage recovery (%)			ambient storage recovery (%)		
0	96.2	97.8	95.8	96.2	97.8	95.8
0	95.5	95.8	97.2	95.5	95.8	97.2
3	94.8	92.7	93.5	95.3	93.2	94.2
7	102.4	99.2	100.7	98.7	97.6	98.1
10	98.9	97.6	97.2	96.3	96.9	97.1
15	97.0	97.8	99.1	99.5	98.1	99.3
20	99.6	98.4	99.6	97.6	98.4	98.1

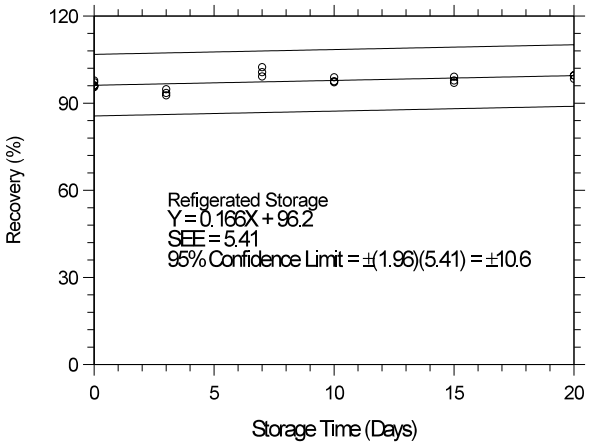

Figure 4.7.2.1. Refrigerated storage test at 1.06 ppm.

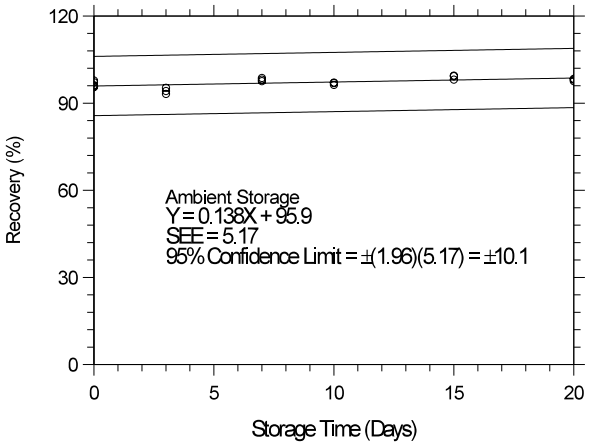

Figure 4.7.2.2. Ambient storage test at 1.06 ppm.

4.8 Reproducibility

Reproducibility samples were prepared by sampling at 1 L/min from two different controlled test atmospheres, one at 9.40 ppb and the other at 1.06 ppm. Both atmospheres were at approximately 80% RH and at room temperatures ranging from 22-26°C. Six samples for each target concentration were submitted to an SLTC service branch for analysis. The samples were stored for 63 and 58 days at 0°C before they were analyzed for the 10-ppb and 1-ppm target concentration samples respectively. One sample at the 9.40-ppb level was much lower than the other samples and is considered to be an outlier. It is suspected that there was a possible leak on the seal of the sample cassette and the manifold adapter used in the controlled test atmosphere generator. The rest of the samples did not deviate greater than the precisions of the overall procedure determined in Section 4.7, which are ±14.8% and ±10.1% for the 10-ppb and 1-ppm target concentrations respectively.

Table 4.8.1
Reproducibility Data for 10-ppb Samples

sample	ng reported	ng expected	percent	deviation
1	2497	2657	94.0	-6.0
2	2319	2524	91.9	-8.1
3	2406	2732	88.1	-11.9
4	2492	2641	94.4	-5.6
5	1880	2780	67.6	-32.4
6	2434	2611	93.2	-6.8

Table 4.8.2
Reproducibility Data for 1-ppm Samples

sample	µg reported	µg expected	percent	deviation
1	340.5	335.5	101.5	+1.5
2	331.8	328.8	100.9	+0.9
3	293.4	308.9	95.0	-5.0
4	340.2	343.2	99.1	-0.9
5	286.4	290.7	98.5	-1.5
6	330.6	332.8	99.3	-0.7

4.9 Extraction efficiency and stability of extracted samples

4.9.1 Extraction efficiency

The extraction efficiencies (EE) for the two levels were determined by injecting standards onto sulfuric acid treated filters with amounts equivalent to 0.05 to 2 times the target concentrations. The average extraction efficiencies over the working range of 0.5 to 2

times the target concentrations are 98.7% and 98.9% based on the 10-ppb and 1-ppm levels respectively.

Table 4.9.1.1
Extraction Efficiency Based on a 10-ppb Target Concentration

× target concn	0.05×	0.1×	0.2×	0.5×	1.0×	2.0×
mass spiked (ng)	157.4	314.7	629.5	1574	3147	6295
EE (%)	98.2	98.4	96.0	98.4	98.2	98.6
	96.1	99.0	96.4	98.6	98.3	98.7
	96.7	97.7	97.0	98.8	98.1	100.4
	96.4	97.0	95.3	99.0	98.3	99.3
	101.5	96.4	96.1	99.0	98.0	99.0
	97.2	96.3	97.1	98.9	97.9	99.0
mean	97.7	97.5	96.3	98.8	98.1	99.2

Table 4.9.1.2
Extraction Efficiency Based on a 1-ppm Target Concentration

× target concn	0.05×	0.1×	0.2×	0.5×	1.0×	2.0×
mass spiked (µg)	15.74	31.47	62.95	157.4	314.7	629.5
EE (%)	98.3	98.5	98.5	98.9	99.3	98.7
	98.2	97.9	98.6	99.0	99.0	98.3
	98.3	97.4	98.6	99.2	99.2	98.3
	98.1	98.2	98.6	99.4	99.0	98.3
	98.3	98.1	98.7	99.5	99.0	98.6
	98.2	97.9	98.4	99.2	98.5	98.5
mean	98.2	98.0	98.6	99.2	99.0	98.4

4.9.2 Stability of extracted and extracted/derivatized samples

The stability of extracted samples at the two target concentrations was investigated by analyzing subsequent aliquots of the extracted samples 24 h after the samples were initially extracted. Three of the extracted samples (the filters were still in the vials) were refrigerated, and the other three were allowed to stand at room temperature on a laboratory bench top for each target concentration. Aliquots of the stored extracts were analyzed with fresh standards. The average percent change was +0.8% and +0.7% for sample extracts that were refrigerated, and +0.3% and +0.3% for those stored at room temperature at the 10-ppb and 1-ppm target concentrations respectively.

Table 4.9.2.1
Stability of Extracted Samples
at the 10-ppb Target Concentration

extracts refrigerated			extracts at room temperature		
initial EE (%)	EE after one day (%)	difference	initial EE (%)	EE after one day (%)	difference
98.2	98.8	+0.6	98.3	98.4	+0.1
98.3	99.0	+0.7	98.0	98.4	+0.4
98.1	99.3	+1.2	97.9	98.3	+0.4
	(averages)			(averages)	
98.2	99.0	+0.8	98.1	98.4	+0.3

Table 4.9.2.2
Stability of Extracted Samples
at the 1-ppm Target Concentration

extracts refrigerated			extracts at room temperature		
initial EE (%)	EE after one day (%)	difference	initial EE (%)	EE after one day (%)	difference
99.3	101.0	+1.7	99.0	99.4	+0.4
99.0	99.2	+0.2	99.0	98.7	−0.3
99.2	99.6	+0.4	98.5	99.3	+0.8
	(averages)			(averages)	
99.2	99.9	+0.7	98.8	99.1	+0.3

The stability of extracted and derivatized samples was investigated by reanalyzing the target concentration samples 24 h after derivatization and initial analyses. After the original analyses were performed, three vials were recapped with new septa while the remaining three retained their punctured septa for each target concentration set. The samples were reanalyzed with fresh standards. The average percent change was −0.4% and −0.2% for samples that were resealed with new septa, and −0.1% and 0.0% for those that retained their punctured septa for samples at the 1-ppb and 10-ppm target concentrations respectively.

Table 4.9.2.3
Stability of Extracted and Derivatized Samples
at the 10-ppb Target Concentration

punctured septa replaced			punctured septa retained		
initial EE (%)	EE after one day (%)	difference	initial EE (%)	EE after one day (%)	difference
98.2	98.2	0.0	98.3	98.0	−0.3
98.3	97.7	−0.6	98.0	98.0	0.0
98.1	97.6	−0.5	97.9	98.1	+0.2
	(averages)			(averages)	
98.2	97.8	−0.4	98.1	98.0	−0.1

Table 4.9.2.4
Stability of Extracted and Derivatized Samples
at the 1-ppm Target Concentration

punctured septa replaced			punctured septa retained		
initial EE (%)	EE after one day (%)	difference	initial EE (%)	EE after one day (%)	difference
99.3	98.7	−0.6	99.0	98.8	−0.2
99.0	99.1	+0.1	99.0	98.8	−0.2
99.2	99.1	−0.1	98.5	98.7	+0.2
	(averages)			(averages)	
99.2	99.0	−0.2	98.8	98.8	0.0

4.10 Qualitative analysis

A UV spectrum for benzalazine was obtained from a Hewlett-Packard 1050 Series programmable variable wavelength detector by injecting a standard using the same conditions given in Section 3.5.1.

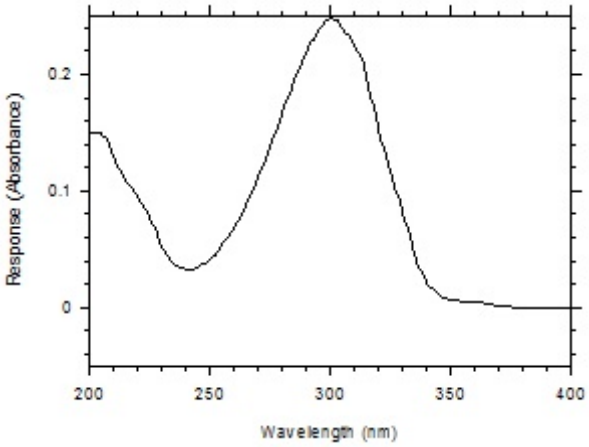

Figure 4.10. UV spectrum of benzalazine in 67/33, acetonitrile/water.

5. References

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