4,4'-METHYLENE-BIS(*O*-CHLOROANILINE) [MOCA]

Method no.:	24
Matrix:	Air
Target concentration:	0.2 mg/m^3 (0.02 ppm) 0.02 ppm is the TLV of the American Conference of Governmental Industrial Hygienists. A skin notation is attached to the standard. The NIOSH recommended standard is 3 µg/m^3 based on a time-weighted average. This value represents the detection limit for this method. (Ref. 5.7.)
Procedure:	Collection in a bubbler containing 15 mL of 0.1 N HCl and analysis by HPLC using UV detection.
Recommended air volume and sampling rate:	100 L at 1 L/min
Reliable quantitation limit:	3.6 µg/m^3
Standard error of estimate at the target concentration: (Figure 4.5.1.)	6.06%
Special requirements:	After air sampling is completed, the inlet tube of the bubbler should be thoroughly rinsed with the fresh collecting solution. The rinse solution should then be combined with the remaining collecting solution for later analysis. (Section 2.3.)
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

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1. General Discussion

1.1. Background

1.1.1. History

A variety of sampling and analytical methods have been employed in the past for monitoring exposure to MOCA. OSHA field samples have been collected using 37-mm cellulose acetate filters, glass fiber filters, and commercially available Florisil and silica gel sorbent tubes. Presently, the most common method employed uses a plastic filter cassette containing a 37-mm Gelman Type A glass fiber filter backed with a cellulose support pad. A two-stage sampling device using a filter and solid sorbent in series has been employed on occasion.

Since 1977 the analysis of MOCA in the OSHA Laboratory has been performed using HPLC. Prior to that time, analysis was performed by the gas chromatographic determination of the fluoroacetyl derivatives using electron capture detection. Analysis of the fluoroacetyl derivatives using FID detection has also been reported in the literature. (Ref. 5.1.)

MOCA is a solid at room temperature and has a relatively low vapor pressure (3.7×10^{-6} mm Hg at 20°C). Industrial applications often employ a molten MOCA process. (Ref. 5.2.) It is believed that an effective air sampling device must be capable of collecting the aerosol and the vapor of MOCA. Recognizing this problem, NIOSH has recommended a two stage sampling device consisting of a 13-mm Gelman Type A glass fiber filter followed by a 50-mg bed of 30/60 mesh silica gel. (Ref. 5.3.)

Rappaport and Morales of the Los Alamos Laboratory, University of California, evaluated this sampling method using an aerosol generation system. (Ref. 5.2.) They concluded that the glass fiber filter quantitatively trapped the MOCA aerosol, and no MOCA was detected on the silica gel backup portion of the sampler. MOCA aerosols from 3.6 to 54.6 $\mu g/m^3$ were generated at relative humidities ranging from 5 to 90%. The ability of the sampler to collect MOCA vapor was not reported in this study. The rationale for recommending silica gel for sampling MOCA vapor was based on the work of Wood and Anderson also from the Los Alamos Laboratory. (Ref. 5.4.) Although MOCA was not evaluated in this study, they found silica gel to be an effective sorbent for the collection of a variety of volatile aromatic amines.

Yasuda, of Los Alamos, reported that Gas Chrom S was an effective solid sorbent for trapping MOCA vapor. (Ref. 5.1.) The vapor in this study was generated by adding a known amount of MOCA to a diffusion chamber contained within a temperature controlled oven. A MOCA concentration of 0.06 µg/L was generated at an oven temperature of 120°C. Gas Chrom S tubes attached directly to the oven outlet resulted in collection efficiencies of 100% for sampling times of 0.5 to 8 h at a 1 L/min sampling rate.

1.1.2. Scope of this study

The evaluation of a MOCA sampling method was pursued in order to develop a reliable collection method for OSHA use. Air sampling over a flask of molten MOCA was performed using a variety of collection methods to test relative collection efficiencies. The design of the sampling apparatus employed did not permit independent determination of the concentration of the MOCA generated, nor could information about the physical state of the MOCA generated be determined. The solid sorbents XAD-2, acid treated and untreated Gas Chrom R, silica gel, Polar Partition and Florisil were tested in this manner. As much as 75% of the MOCA collected was found on the glass wool plug at the front of the tube when SKC silica gel, SKC Polar Partition, and hand-packed Gas Chrom R tubes were tested. Analysis of the individual portions of SKC XAD-2 and Florisil tubes indicated that the glass wool plugs on the ends and in the middle of the tube collected MOCA more effectively than the sorbent. Although the sorbent tubes tested may be effective in trapping MOCA at low levels, at the high loadings generated in this study, (10 to 100 µg) they were not effective.

When relatively dry laboratory air was drawn through the apparatus, 37-mm Gelman glass fiber filters, untreated and treated with 0.05 N H_2SO_4 were effective in trapping MOCA over the molten state. When an aqueous bubbler was attached to the molten MOCA system so that wet air was being sampled, the acid treated filter was less effective in trapping

MOCA. Considerable amounts of MOCA were detected on the cellulose support pad in this case.

The initial results of this study indicated that a glass fiber filter followed in series with a silica gel tube might be an effective sampling method. However, it was later determined that low recoveries were obtained when MOCA was spiked onto glass fiber filters and air was drawn through the system. Similar low recoveries were also observed with air drawn through MOCA spiked silica gel, Gas Chrom R or XAD-2 solid sorbents. This loss of MOCA was apparently not due to volatilization since no MOCA was detected in any backup system, but was probably due to decomposition. Similar phenomena have been observed in our laboratory with benzidine. (Ref. 5.5.) Reports of oxidation of aromatic amines stored on silica gel have been reported in the literature. (Ref. 5.4.)

In breakthrough studies of MOCA, it was observed that the degree of decomposition or oxidation was not simply a function of the air volume sampled through the collection media. The recovery from spiked glass fiber filters, with equal volumes of air sampled, varied from approximately 46 to 99% with either dry laboratory air or 70 to 80% relative humidity air. Similar results were observed for silica gel, Gas Chrom R and XAD-2 solid sorbents. MOCA spiked into open glass vials (2.5 µL × 1523 µg/mL MOCA standard in methanol) and left exposed to the air for 24 hours both in room light and in the dark resulted in average recoveries of 87.5% and 89.5% respectively for triplicate 3.8 µg spikes. One-hundred percent recoveries were consistently obtained only if the MOCA was spiked into the methanol desorbing solution containing the sampling media.

In an attempt to determine if the loss of MOCA was due to oxidation, nitrogen was passed through a sodium metal-ketyl mineral oil oxygen scrubbing system and drawn through spiked filters. No improvement in recovery was noted. It is possible that the oxygen was not completely removed from the system or that decomposition occurred during the spiking process. Further efforts to evaluate this phenomenon were not undertaken.

Storage studies were conducted for glass fiber filters, cellulose backup pads, silica gel tubes, and 0.1 N HCl aqueous bubbler solutions. The results indicate that no further degradation occurs for filters after the initial loss. Further degradation is observed however for backup pads and silica gel tubes stored both at 4°C and ambient conditions. No degradation is observed with storage for the 0.1 N HCl bubbler solution.

Because of the problems encountered with glass fiber filters and solid sorbents, the 0.1 N HCl bubbler was selected as the sampling device for MOCA. This sampling procedure passes all of the criteria established by the Methods Evaluation Branch.

In order to further evaluate the efficiency of the bubbler as a sampling method, comparative sampling over molten MOCA was conducted.

Two 0.1 N HCl bubblers connected in series were attached to one side of a sampling arm, and a glass fiber filter-silica gel sampling train was attached to the other side. Moist air was drawn past the molten MOCA, generating average air concentrations ranging from 0.062 to 0.43 mg/m^3 as determined by the analysis of the bubbler sampling system. Although equal volumes of moist air were drawn through both sides of the sampling apparatus, low recoveries of MOCA for the filter-silica gel system relative to the bubbler system were obtained in three of four experiments. In no case was MOCA recovery for an alternate sampling method found to exceed the 0.1 N HCl aqueous bubbler. In addition, it was determined that one bubbler was efficient in trapping MOCA at the levels generated.

It is recognized that some convenience in sampling is sacrificed with the use of a bubbler. It is also recognized that there are inherent limitations in this evaluation process. For this reason it is believed that side by side field sampling will provide valuable information regarding the relative collection efficiency of the bubbler versus the filter-silica gel sampling system.

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

Like other aromatic amines, MOCA can produce a cyanotic-anemic syndrome if absorbed into the body in high levels. However, MOCA may be classified as only mildly cyanogenic relative to p-chloroaniline as measured by its ability to produce methemoglobinema in humans. (Ref. 5.6.)

Of greater concern is the evidence that MOCA is a carcinogen as indicated by five separate animal studies using rats, mice, and dogs. (Ref. 5.7.) In a NIOSH-conducted study, a dose relationship of cancer to MOCA levels in the diet of rats was observed. MOCA levels ranging from 125 to 1000 ppm in a protein adequate and a protein deficient diet were fed to two groups of rats over an 18-month period. Although there was a variation in the incidence of various types of tumors between the two groups, both MOCA exposed groups had an increased incidence of malignant tumors compared to control groups. (Ref. 5.7.)

In another study, continuous daily oral doses of 8 to 15 mg/kg of MOCA administered to female beagles for up to nine years produced evidence of urinary bladder cancer in three of five dogs. No cases were observed in six controls. (Ref. 5.7.)

A positive Ames test for MOCA has also been demonstrated using Salmonella Typhimurium indicating that MOCA is mutagenic in an in vitro system. (Ref. 5.7.)

Evaluation of human exposure to MOCA is limited to one study conducted by DuPont on 209 employees who were exposed to MOCA over a 15-year period at their Chamber's Works facility. (Ref. 5.6.) Urinary MOCA levels as high as 25 mg/L were reported before controls were initiated. Maximum levels after controls range from 1.6 to 6.7 mg/L in a group of 17 current workers. These urinary levels are higher than expected based on the air concentration levels measured at the facility. The authors suggest that this may indicate that skin absorption is a major route of entry.

Some pathological disorders in urinary tract cells were observed among the 209 current or former employees as determined by the Papanicolaon (Pap) technique. Of 178 former employees two deaths due to cancer were reported. According to the report, the overall average cancer death rate for a 15-year period at the Chamber's Works facility which includes all 6500 employees is lower than the national average. (Ref. 5.6.)

1.1.4. Exposure

MOCA is used as a curing agent in the production of polyurethane elastomers. Hard tires, rollers, seals, crash pad foam and vibration dampeners are products produced from urethane elastomers. It is estimated that 3.3 million kg of MOCA were produced in 1972. (Ref. 5.2.)

NIOSH reports that in the early 1970s approximately 55,000 U.S. workers were potentially exposed to MOCA. (Ref. 5.7.)

1.1.5. Physical properties (Ref. 5.7.)

CAS no.:	101-14-4
synonyms:	Bis Amine, Curalin M., Curene 442 3,3'-dichloro-4,4'-diaminodiphenyl methane
physical properties :	Yellow to tan pellets, nearly odorless.
melting point:	99-107°C
solubility:	Slightly soluble in water. Soluble in alcohol, ketones, esters and many organic solvents.
vapor pressure:	3.7×10^{-6} mm Hg at 20°C (Ref. 5.2.)
specific gravity:	1.44 at 24°C
chemical formula:	$C_{13}H_{12}N_2C_{12}$
molecular weight:	267.16

1.2. Limit defining parameters

1.2.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure is 0.48 ng of MOCA per injection. This is the amount of analyte which will give a peak whose height is approximately five times the amplitude of the baseline noise. (Section 4.1.)

1.2.2. Detection limit of the overall procedure

The detection limit of the overall procedure is 0.36 µg per sample (3.6 µg/m^3). This is the amount of analyte spiked in the sampling device which allows recovery of an amount of analyte equivalent to the detection limit of the analytical procedure. (Section 4.1.)

1.2.3. Reliable quantitation limit

The reliable quantitation limit is 0.36 µg per sample (3.6 µg/m^3). This is the smallest amount of analyte which can be quantitated within the required 95% confidence limits of ±25%. (Section 4.1.)

The reliable quantitation limit and detection limits reported in this method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

1.2.4. Sensitivity

The sensitivity of the analytical procedure over a concentration range representing 0.5 to 2 times the target concentration is 53,542 area units per µg MOCA/mL. The sensitivity is determined from the slope of the calibration curve. Variations in sensitivity may be observed with different instruments. (Section 4.2.)

1.2.5. Precision (analytical method only)

The pooled coefficient of variation obtained from replicate determinations of analytical standards at 0.5, 1, and 2 times the target concentration is 0.0282. (Section 4.4.)

1.2.6. Precision (overall procedure)

The overall procedure must provide results at the target concentration that are ±25% or better at the 95% confidence level. The precision at the 95% confidence level is 14.4% for the 21-day storage test. This includes an additional ±5% for sampling error. (Section 4.5., Figure 4.5.1.)

1.3. Advantages

1.3.1. The analytical procedure is rapid, sensitive, and reproducible.

1.3.2. Direct injection of sample is used for the analysis since no derivatization steps are required.

1.3.3. Reanalysis of samples is possible.

1.4. Disadvantages

1.4.1. Bubbler collection solutions are cumbersome to use. Loss of sample can easily occur.

1.4.2. Detection limits for bubbler solutions are greater than filters or sorbent tubes since the sample is more dilute.

1.4.3. The sampling procedure has not been field tested.

2. Sampling Procedure

2.1. Apparatus

2.1.1. An air sampling pump with a flow rate which can be calibrated to within ±5% of the recommended 1 L/min flow rate while the sampler is in line.

2.1.2. Clean, dry 25-mL glass bubblers, fitted with matched ground glass joints and a fritted glass inlet.

2.1.3. Clean, dry 20-mL glass scintillation vials fitted with leakproof Polyseal caps or other suitable glass containers for transporting samples.

2.1.4. Glass Pasteur type pipettes equipped with small rubber bulbs for rinsing the bubbler, etc., and transferring the collection solution.

2.2. Reagents

0.1 N Hydrochloric acid collecting solution.

2.3. Sampling technique

2.3.1. Place 15 mL of the 0.1 N HCl aqueous solution into a clean, dry bubbler. Connect the bubbler to the sampling pump using flexible tubing, and maintain the device in an upright position throughout the sampling period. Fifteen milliliters of solution is an adequate volume for at least 5 h of sampling at 25°C.

2.3.2. After having completed sampling, transfer the entire contents of the bubbler to the scintillation vial for shipping to the laboratory. Rinse the inlet tube of the bubbler and the bubbler with several small volumes of fresh 0.1 N HCl solution and add these rinses to the shipping vial.

2.3.3. Insure that the vial is leakproof, and sealed with the properly labeled OSHA seal.

2.3.4. Avoid unnecessary exposure of the sample to direct light and/or heat.

2.3.5. Include all necessary paper work with the samples for shipping to the laboratory. Insure that all possible interferences or other pertinent information is included.

2.3.6. Submit any bulk samples in sealed containers under separate cover.

2.4. Breakthrough

2.4.1. Retention efficiency

Three bubblers containing 15 mL of 0.1 N HCl solution were spiked with 5.87 µg of MOCA in methanol. Ninety-two liters of air at 72% relative humidity was drawn through the bubblers at 1 L/min. The average recovery for the three bubblers was 101%. The average recovery for a 117.5 µg spike of MOCA was 97% in a similar study. (Section 4.6.) Low recoveries on glass fiber filters were observed in similar studies. (Section 4.7.)

2.4.2. Collection efficiency

In order to evaluate the collection efficiency of MOCA, air was sampled over a flask of molten MOCA using an apparatus diagrammed in Figure 4.6.

Air concentrations of MOCA generated ranged from 0.062 to 0.43 mg/m^3 as determined by the analysis of the bubbler system.

With the exception of the 205-L sampling, higher recoveries were found with the bubbler system in all four studies each performed on different days. No MOCA was detected on any of the back sections of silica gel. No MOCA was detected on the connecting piece of the two bubblers. The amount of MOCA found in the second bubbler was relatively small in all four cases.

The results of this experiment must be viewed with caution. The actual amount, as well as the physical state of the MOCA generated, is not known. In two of the four comparative samplings, the sections of tubing connecting the glass Y tube to the sampling device were rinsed with methanol and analyzed for MOCA. For the 205-L air sample, 9.07 µg was found on the filter side, and 7.6 µg on the bubbler side. For the 142-L air sample, 57.6 µg was found on the filter side, and 68.5 µg on the bubbler side.

These results indicate that both sides of the sampling device are apparently being exposed to a similar MOCA atmosphere. It is possible that the difference in recovery for the filter assembly is due to oxidation or decomposition. (Section 4.8.)

2.5. Recommended air volume and sampling rate

2.5.1. The minimum recommended air volume is 100 L.

2.5.2. The recommended sampling rate is 1 L/min.

2.6. Interferences

There are no known interferences involved in the sampling procedure.

2.7. Safety precautions

2.7.1. Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

2.7.2. Follow all safety practices that apply to the work area being sampled.

3. Analytical Procedure

3.1. Apparatus

3.1.1. High performance liquid chromatograph equipped with pump, sample injector, UV detector, chart recorder and necessary hardware.

3.1.2. HPLC analytical column capable of separating aromatic amines. A 25-cm × 4.6-mm stainless steel column, slurry packed with Zorbax ODS 8-µm spherical packing material was used for this analysis.

3.1.3. An electronic integrator, or other suitable method to measure detector response.

3.1.4. Microliter syringes or automatic sampling device for making sample injections.

3.1.5. Volumetric glassware for sample and standard preparations.

3.1.6. A pH meter or pH indicating paper for adjusting pH of collecting solution to neutral conditions.

3.2. Reagents

3.2.1 HPLC grade methanol.

3.2.2. HPLC grade water. Our laboratory uses a commercially available water filtration system for the preparation of HPLC grade water.

3.2.3. Sodium hydroxide, reagent grade.

3.2.4. Purified MOCA standard. (Section 3.3.1.)

3.3. Standard preparation

3.3.1. HPLC analysis of technical grade MOCA standards at 254 nm indicates the presence of contaminants. A cyclohexane extraction method for purification of MOCA gave low recoveries and was found to be time consuming. (Ref. 5.2.) In lieu of this method a semi-preparative HPLC method was used to purify the MOCA standard. Fifty-microliter injections of Pfaltz and Bauer technical grade MOCA in methanol were made onto a 50 cm long Whatman Magnum Partisil ODS column using a methanol-water mobile phase. Approximately 50 mg was loaded onto the column per injection without serious loss of peak shape. Using UV detection, the major peak was collected. A portion of each fraction collected was reinjected onto an analytical column under similar conditions to assure purity. Heptane was then added to the pooled fractions and the methanol and water mobile phase removed by rotary evaporation. Approximately 0.8 g of MOCA was obtained by this method. The melting point of the purified MOCA was 108.5-109.5°C. The melting point of the technical grade MOCA was 102-108.5°C. The purified standard is nearly white in appearance compared to the tan colored technical grade MOCA. No contaminants were detected by GC/MS in the purified MOCA. The

unpurified standard was calculated to be approximately 95-98% pure relative to the purified standard.

3.3.2. Stock standards of MOCA are prepared by weighing a portion of the purified MOCA standard into HPLC grade methanol. These solutions stored in dark bottles in a refrigerator are stable for an indefinite period of time. Working range standards (0.02 to 10 µg/mL) are prepared by making dilutions of the stock solution into HPLC grade water. These dilute MOCA standards in water are also quite stable, although decomposition of dilute standards in methanol has been observed. (Section 3.6.6.)

3.4. Sample preparation

3.4.1. Neutralize the 0.1 N HCl collecting solution with several drops of saturated NaOH. Check the pH with pH paper or a pH meter.

3.4.2. Measure and record the total volume of the collecting solution with a graduated cylinder.

3.5. Analysis

3.5.1. HPLC conditions

column:	Zorbax ODS 8-µm stainless steel column (25 cm × 4.6 mm)
mobile phase:	methanol/water 80:20 (v/v)
flow rate:	1 mL/min
UV detector:	254 nm or 280 nm
injection volume:	20 µL
retention time:	approximately 6 min

3.5.2. Use of a dual wavelength detector permits simultaneous detection at an alternate 280 nm wavelength. Since UV response varies with wavelength, this information can be useful for confirmatory purposes as well as for the recognition of interferences. A UV scan of the purified MOCA standard in methanol is shown in Figure 4.7.

3.5.3. A representative chromatogram is shown in Figure 4.3.

3.5.4. Detector response is measured by electronic integration.

3.5.5. An external standard procedure is used for quantitation. A calibration curve of at least three different MOCA concentrations is used. Although the MOCA response is linear over a broad concentration range, it is good laboratory practice to bracket the sample values with standards.

3.6. Interferences

3.6.1. There are no known interferences to MOCA which cannot be resolved by changes in mobile phase conditions.

3.6.2. 2,4-Toluenediamine and methylenebisdianiline, the hydrolysis products of the 2,4-TDI and MDI diisocyanates, are not interferences.

3.6.3. Benzidine, α and β-naphthylamine, and o-toluidine are not interferences.

3.6.4. 4-Amino-diphenyl (4-ADP) and dichlorobenzidine (DCB) elute with the same retention time as MOCA under the recommended analytical conditions. With dual wavelength detection at 254 nm and 280 nm, these interferences can be readily recognized since their absorbance ratios differ markedly from MOCA. By adjusting the mobile phase to methanol/water 75:25 (v/v), MOCA is separated from 4-ADP and DCB. 4-ADP and DCB elute at 9.6 min and MOCA at 10.5 min under these conditions.

3.6.5. A matrix effect for MOCA in a mixture of aromatic amines has been observed. In an amine standard mixture MOCA elutes slightly earlier than if it is analyzed separately.

In order to identify MOCA in a complex sample, it may be necessary to spike a portion of the field sample with MOCA and reanalyze.

3.6.6. In the course of this study, it was observed that some standards and spiked samples stored in methanol had decomposed with time. Since this decomposition has not been observed for samples or standards in water, the problem appears to apply only to the analysis of samples dissolved in methanol. The nature of this decomposition in methanol is not understood. One of the decomposition products may co-elute with MOCA at the specified analytical conditions. This decomposition product is observed at 254 nm but not at 280 nm. With dual wavelength detection, this problem can be recognized by peak ratioing. Adjustment of the mobile phase to methanol/water 75:25 (v/v) will separate MOCA from this decomposition product. In the event that only 254 nm is being monitored, the recommended analytical conditions should only be used to screen samples. Reanalysis at the alternate mobile phase conditions may be necessary. (Figure 4.8.)

3.7. Calculations

3.7.1. A linear least-squares fit is determined using standard concentrations and response values. Sample response values are used to determine the sample concentration from the least squares fit of the standards.

3.7.2. The air concentration for a sample in $\mu g/m^3$ is determined from the following formula:

$$\mu g/m^3 = \frac{(\mu g / mL\ MOCA\ in\ sample) \times (total\ mL\ of\ collecting\ solution)}{Air\ volume\ in\ cubic\ meters}$$

3.8. Safety precautions

3.8.1. Sample and standard preparations should be performed in a fume hood. Avoid exposure to both standards and samples.

3.8.2. Avoid all possible skin contact with MOCA.

3.8.3. Confine the use of solvents to a fume hood.

3.8.4. Wear safety glasses in all laboratory areas.

3.8.5 MOCA should be handled with extreme care since it is an animal carcinogen.

4. Backup Data

4.1. Detection limits

4.1.1. The analytical detection limit for MOCA is 0.48 ng per injection (20 µL × 0.024 ng/µL). This amount of analyte gave a peak whose height was approximately five times the amplitude of the baseline noise. (Figure 4.1.)

4.1.2. The overall detection limit of the procedure is 0.36 µg per sample (0.024 µg/mL × 15 mL).

4.1.3. The reliable quantitation limit is the same as the detection limit of the overall procedure since the precision at the detection limit is better than ±25% at the 95% confidence level. This was determined with replicate 20-µL injections of a 0.024 µg/mL MOCA in water standard.

Table 4.1.3.
Reliable Quantitation Limit Data

peak height (mm)	statistics
4.2	
4.5	$\bar{x}$ = 4.47
4.8	SD = 0.207
4.3	CV = 4.63%
4.5	±1.96(CV) = ±9.1%
4.5	

4.2. Sensitivity

The calibration curve for MOCA is shown in Figure 4.2. The slope of the regression line is a measurement of the sensitivity of the analytical method.

4.3. Chromatogram

A typical chromatogram for MOCA is presented in Figure 4.3.

4.4. Precision of the analytical method

MOCA standards at 0.5, 1 and 2 times the target concentration were each injected five times using a Waters WISP automatic sampler. The area response for each injection was measured by electronic integration and the results used to construct a calibration curve. The calculated best fit values in µg/mL of each injection are used to determine a pooled coefficient of variation.

Table 4.4.
Precision of the Analytical Method

× target conc µg/mL	.0.5× 0.609	1× 1.218	2× 2.43
µg/mL found	0.615	1.183	2.416
	0.621	1.231	2.436
	0.618	1.215	2.306
	0.610	1.198	2.481
	0.580	1.261	2.510
$\bar{x}$	0.609	1.218	2.430
SD	0.0166	0.0302	0.0784
CV	0.0273	0.0248	0.0320

$\overline{CV}$ = 0.0282

4.5. Storage

The percent recovery of MOCA after storage in aqueous 0.1 N HCl collecting solution is reported in Table 4.5. Thirty-six samples were prepared for storage by spiking 15 mL of collecting solution contained in 20-mL glass scintillation vials with 14.6 µg of MOCA (9.6 µL × 1523 µg/mL). Six samples were analyzed immediately. Of the remaining 30 samples, half were stored at room temperature in a laboratory drawer and the other half were stored in a refrigerator at -5°C. At the indicated time intervals, three samples each were removed from storage and analyzed for MOCA. The results of the ambient and the refrigerated storage are presented in Figures 4.5.1. and 4.5.2.

Over the same time period a similar storage study was conducted with MOCA spiked on glass fiber filters, cellulose support pads, and the front silica gel sections of the SKC sorbent tubes. All of these sampling media were spiked with MOCA and stored in 4-mL glass Waters WISP vials. Both ambient and refrigerated storage were conducted at the indicated time intervals. The samples were desorbed with methanol and analyzed. The results of both ambient and refrigerated storage for glass fiber filters, support pads, and silica gel are presented in Figures 4.5.3. through 4.5.8.

Recoveries of MOCA on the filter are constant after the initial loss upon spiking. A further loss of MOCA is observed for cellulose support pads and silica gel stored at both ambient and refrigerated conditions. No losses are observed on day zero for controls of spiked methanol solutions on each of the sampling media.

Table 4.5.
Storage Tests

storage time (days)	% recovery (refrigerated)			% recovery (ambient)		
0	102.0	102.0	103.0	97.1	94.0	102.0
4	101.0	104.0	102.0	105.0	97.1	104.0
7	102.0	106.0	107.0	107.0	107.0	110.0
11	97.1	102.0	103.0	102.0	104.0	102.0
18	103.0	103.0	103.0	100.0	97.1	101.0
21	93.3	103.0	112.0	93.0	97.1	95.2

4.6. Bubbler retention efficiency

4.6.1. Four bubblers containing 15 mL of aqueous 0.1 N HCl were spiked with 8.75 µg of MOCA (5 µL × 1.75 µg/mL) in methanol. Three of the bubblers were placed on the humid air generator and 92 L of air at 72% relative humidity was drawn through each bubbler at 1 L/min. No air was drawn through the fourth bubbler (control). The percent recovery of MOCA from the four bubblers was 103.0, 100.0, 100.0, and 99.0 (control).

4.6.2. A similar study was done with a 117.5-µg spike of MOCA into 15 mL of 0.1 N HCl collecting solution. One hundred and thirty-three liters of air at 78% relative humidity was drawn through each bubbler at 1 L/min. The percent recovery of MOCA from the four bubblers was 94.0, 98.5, 99.0 and 97.4 (control).

4.7. Glass fiber filter retention efficiency

4.7.1. The average recovery for 12 glass fiber filters spiked with either 4.77 µg or 5.96 µg MOCA on different days was 80%. The recoveries ranged from a low of 45% to a high of 99%. Air volumes used ranged from 60 to 68 L. Both relatively dry laboratory air and 80% relative humidity air was used at a flow rate of 1 L/min. No correlation was observed between the percent recovery and the volume or the relative humidity of the air sampled. (Table 4.7.)

4.7.2. To examine sample loss from a glass fiber filter, a cassette containing a spiked glass fiber filter was backed by a bubbler containing 15 mL of 0.1 N HCl. Three filters were spiked with 117.5 µg of MOCA and 147 L of humid air was sampled. No MOCA was detected in any of the three bubbler backup systems although the average loss from the filters was 18%. MOCA was also not detected in cassette rinses, or on connecting pieces to the bubbler.

Recoveries for spiked XAD-2, Gas Chrom R and silica gel are similar to glass fiber filters. Similar conditions were used for the solid sorbents as was employed in the above work.

Table 4.7.
Retention Efficiency
of Spiked Glass Fiber Filters at Ambient Conditions

amount spiked (µg)	recovered (µg)	percent recovery	air volume (L)	relative humidity
5.96	4.28	71.8	68	5%
	4.37	73.3	68	
	5.35	89.8	68	
	5.60	93.9	0	
5.96	4.99	83.7	60	75%
	5.67	95.1	60	
	4.87	82.0	60	
	6.8	114.0	0	
5.96	2.74	45.9	60	75%
	5.50	92.3	60	
	5.88	98.6	60	
	6.60	111.0	0	
4.77	3.21	67.3	60	80%
	4.13	86.6	60	
	3.46	72.5	60	
	4.34	90.9	0	

4.8. Collection efficiency

A 125-mL flat bottomed boiling flask containing several grams of technical grade MOCA was maintained in a molten state using a heating mantel equipped with a rheostat. A two holed rubber stopper fitted with unequal lengths of glass tubing was placed into the top of the flask. The longer piece of tubing extended to a point near the surface of the molten MOCA. The shorter piece of tubing served as an inlet to the flask. To achieve humid air sampling conditions a bubbler containing 15 mL of water was attached to the inlet tube with flexible tubing. To the outlet tube was attached a 10-cm piece of tubing. Samplers were attached directly to this piece of tubing for testing individual sampling devices. For sampling with two devices, a glass Y with two 15-cm lengths of flexible tubing arms was attached to the outlet tubing section. Samplers were attached directly to each of the tubing arms for comparative sampling. The apparatus was

supported by means of a ring stand and clamps. A schematic of this apparatus is shown in Figure 4.6. Air was drawn through the sampling devices using either a Gast pressure/vacuum pump or a personal sampling pump attached with flexible tubing. Flow rates were controlled by means of critical orifices or individual sampling pumps. The separate flow rates and total flow rates through the system were determined before, during, and after sampling. The sum of the individual flow rates equaled the total flow for the system.

The collection efficiency of two 15-mL 0.1 N HCl bubblers in series was measured against the collection efficiency of a glass fiber filter-silica gel sampling system. The bubbler sampling train consisted of two glass bubblers, each containing 15 mL of 0.1 N HCl, connected in series with a piece of flexible tubing. The filter assembly consisted of a two piece plastic cassette containing a 37-mm Gelman type A glass fiber filter with a Millipore cellulose backup pad for support. An SKC silica gel tube (6 mm × 70 mm) containing a 150-mg front and a 75-mg back section was attached to the outlet of the cassette with a short piece of flexible tubing and a plastic SKC cap with the end removed. The tube was butted against the cassette outlet to minimize exposed tubing. For comparative sampling over the molten MOCA, both sampling systems were used to sample for the same period of time at 1 L/min. After sampling was completed, the filter assembly sampling components were immediately desorbed with methanol. Analysis of the individual components of each sampling system was performed within 24 h of collection. The glass fiber filter, backup pad, front and back portions of silica gel, including front glass wool section, empty silica gel tube, plastic cassette and connecting tubing were all desorbed with methanol and analyzed for MOCA using a standard of MOCA prepared in methanol. The inlets of both glass bubblers were rinsed with a portion of the collecting solution. The 0.1 N HCl collecting solution was neutralized with several drops of saturated NaOH solution and analyzed directly for MOCA using a standard of MOCA in water. The results of this experiment are shown below.

Table 4.8.
Comparative Sampling Over Molten MOCA

amount found in filter-silica gel assembly (µg)						amount found in bubbler assembly (µg)		
air volume (L)	glass fiber filter	support pad	silica cassette	silica gel tube	total	first bubbler	second bubbler	total
142	18.02	0.85	13.14	0.882	32.89	57.65	3.33	60.98
143	15.88	3.11	4.17	0.59	23.75	39.43	3.47	42.90
205	9.51	2.13	4.70	1.30	17.64	18.75	0.60	19.35
206	3.07	0.38	2.20	ND	5.65	11.70	0.78	12.72

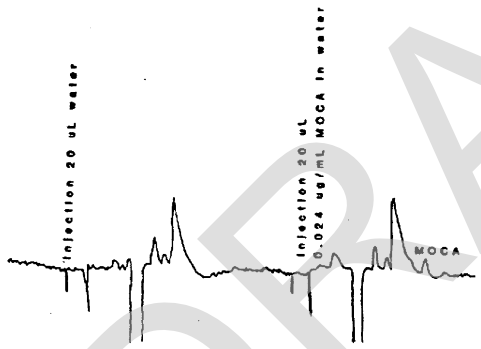

Figure 4.1. Detection limit for MOCA.

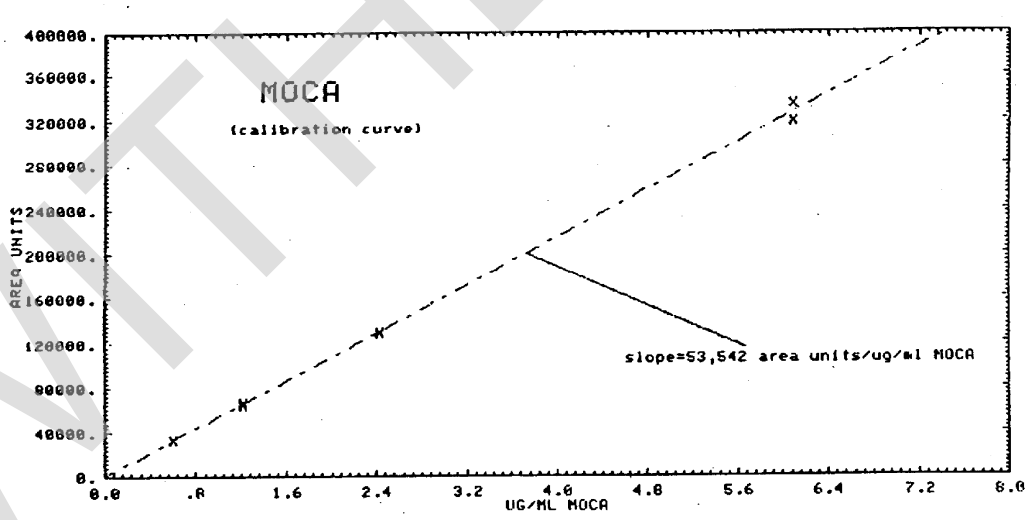

Figure 4.2. Calibration curve for MOCA.

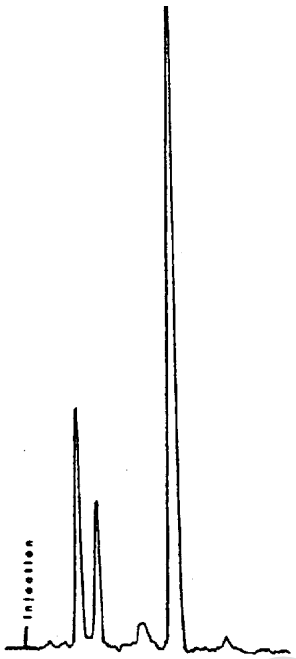

Figure 4.3. Chromatogram of MOCA standard.

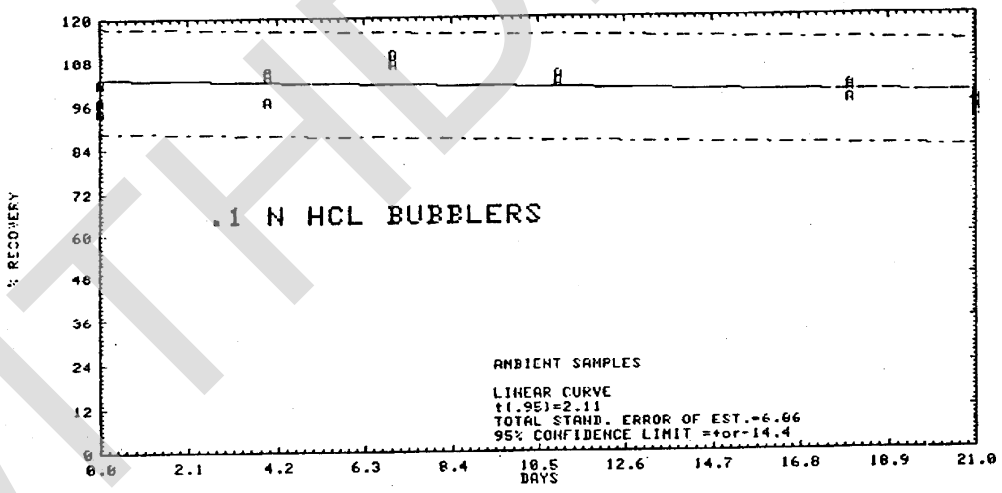

Figure 4.5.1. Ambient storage of MOCA in acid.

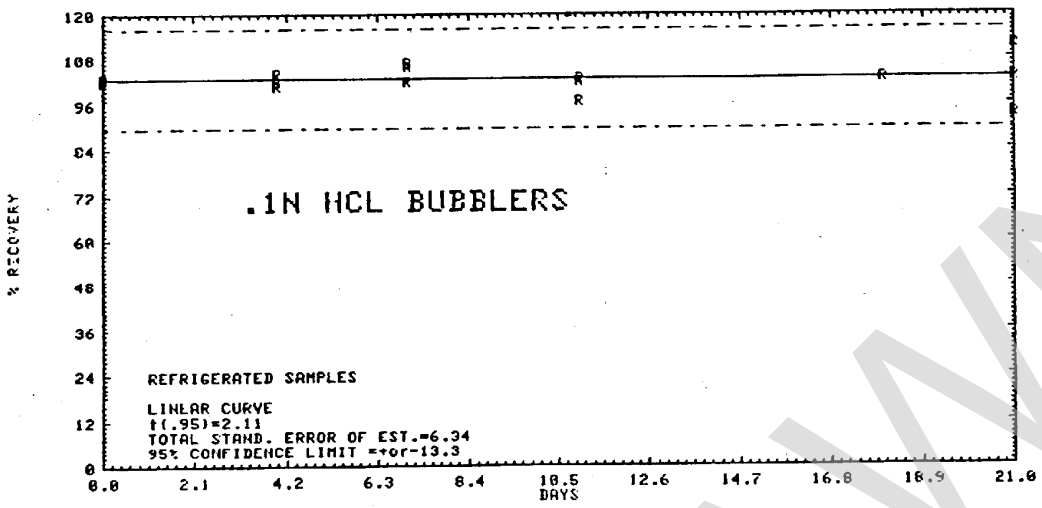

Figure 4.5.2. Refrigerated storage of MOCA in acid.

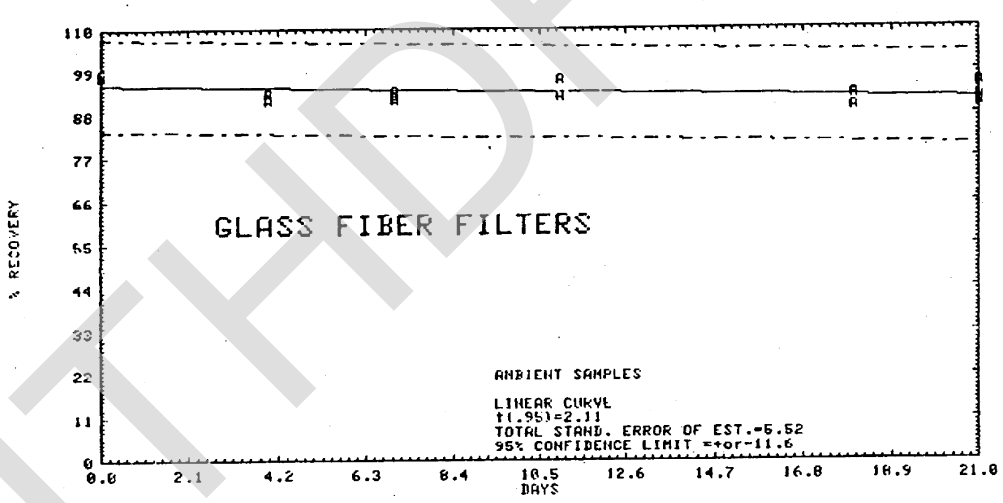

Figure 4.5.3. Ambient storage of MOCA on glass fiber filters.

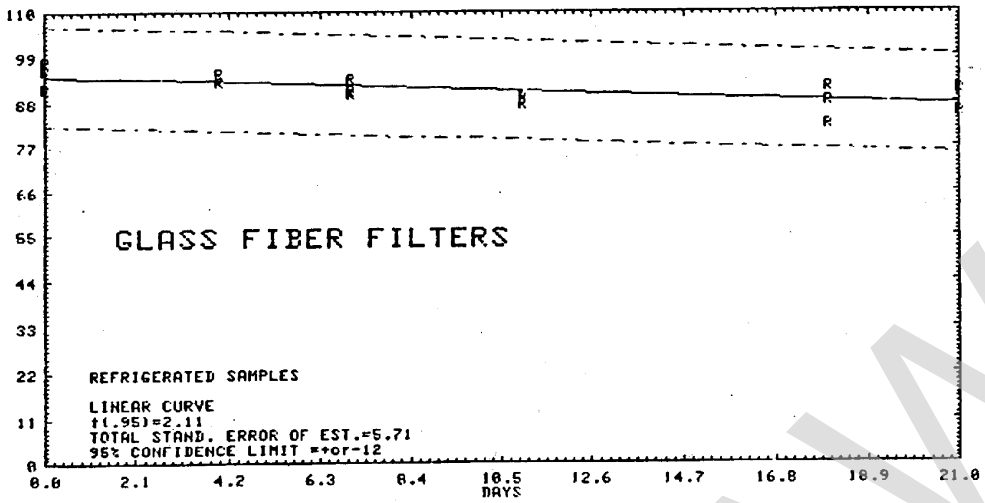

Figure 4.5.4. Refrigerated storage of MOCA on glass fiber filters.

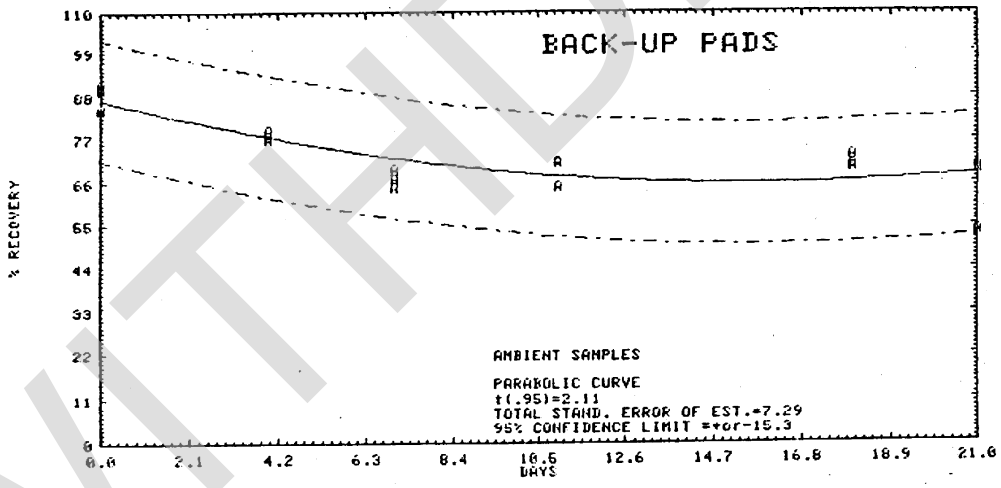

Figure 4.5.5. Ambient storage of MOCA on back-up pads.

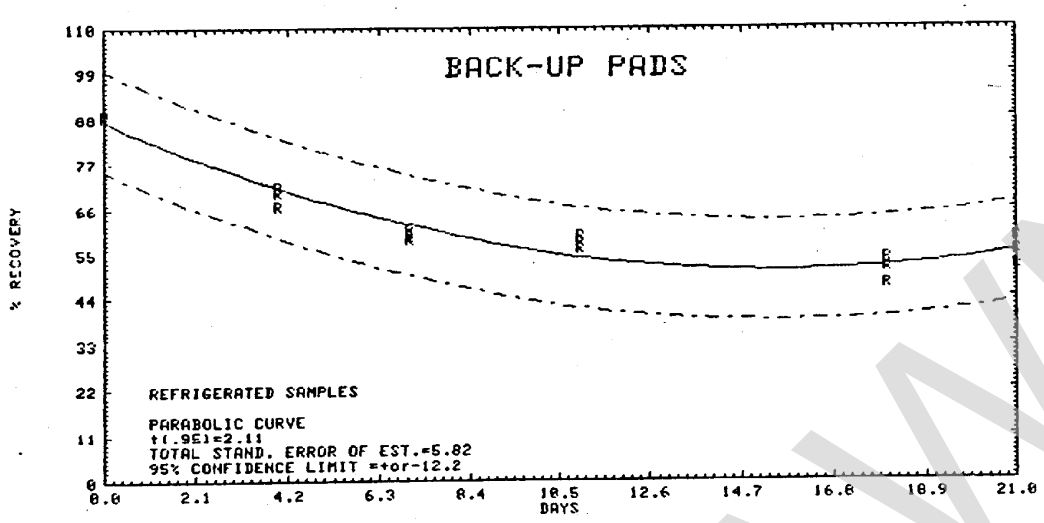

Figure 4.5.6. Refrigerated storage of MOCA on back-up pads.

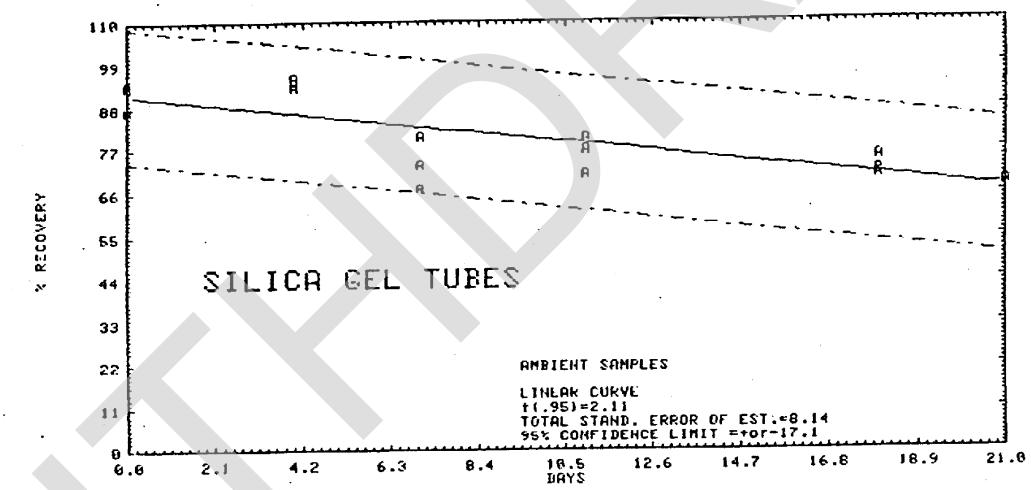

Figure 4.5.7. Ambient storage of MOCA on silica gel.

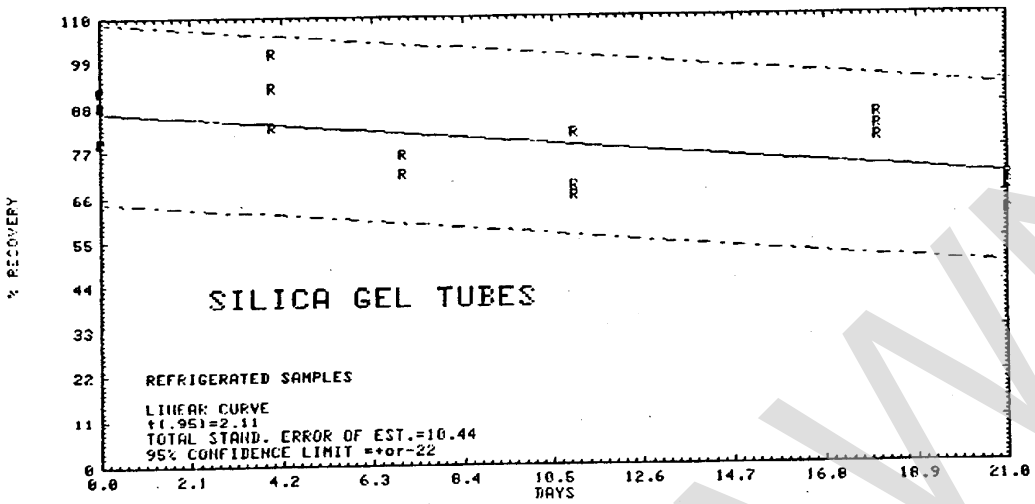

Figure 4.5.8. Refrigerated storage of MOCA on silica gel.

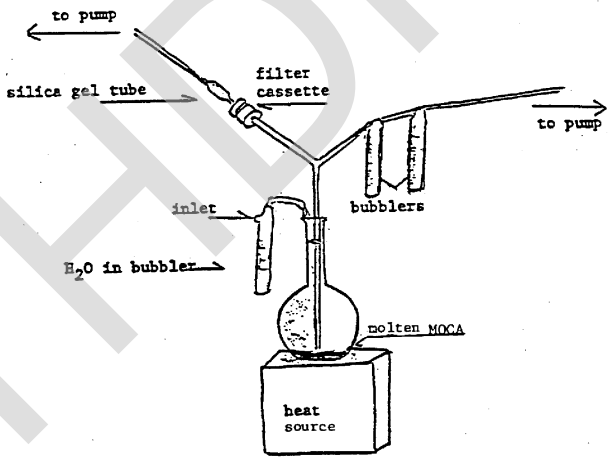

Figure 4.6. Sampling apparatus for MOCA.

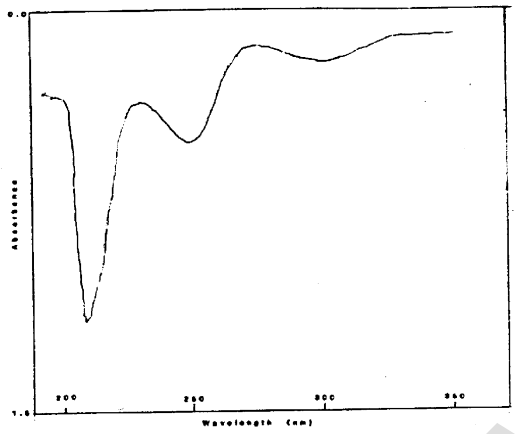

Figure 4.7. UV spectrum of MOCA in methanol.

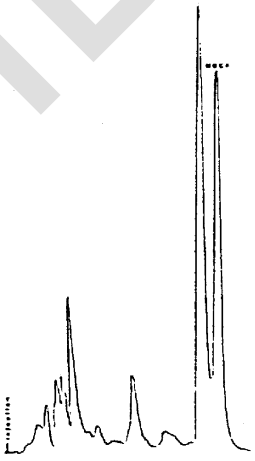

Figure 4.8. Chromatogram of MOCA in the presence of decomposition products.

5. References

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