# Failure Report No. S157

PB81240665

Substance: Acrylamide

OSHA Standard: 0.3 mg/cu m

Chemical Used: Acrylamide from Matheson, Coleman, and Bell

## Methods Attempted

Collection of acrylamide on a solid sorbent or in a midget impinger containing water was investigated. Organic solvents and water were used for desorbing acrylamide from the solid sorbents. Gas chromatography, using a flame ionization detector, was used for analysis of acrylamide.

Two derivatization methods were attempted. The first was a Diels-Alder reaction with 1,3-cyclohexadiene. The second was a reaction with morpholine. Gas chromatography, using a flame ionization detector, was used for analysis of the reaction products.

## Reasons for Failures

The solid sorbent approach was abandoned, because the pressure drop across a tube containing Tenax GC was too high at the flow rate required to collect a sufficient amount of acrylamide for gc analysis.

In the case of collection in a midget impinger, a gas chromatographic column that would give adequate sensitivity and would withstand repeated injections of acrylamide in water could not be found.

The Diels-Alder reaction with 1,3-cyclohexadiene did not appear to be complete after 24 hours, and these tests were discontinued. The morpholine derivative could not be gas chromatographed.

## Discussion

Desorption efficiency trials were performed on several solid sorbents. A desorbing solution of 10% acetone in carbon disulfide was chosen in order to minimize detector response to the desorbing solvent so that adequate separation between solvent tail and acrylamide could be achieved. Each sorbent was spiked with 36 micrograms of acrylamide, which is the amount of acrylamide present at 1X the OSHA standard level based on a sample volume of 120 liters. This is the minimum amount of acrylamide required for adequate gc sensitivity. Each sample was desorbed in 1 ml of 10% acetone in carbon disulfide and analyzed by gc, using flame ionization detection. A 6-ft x 1/8-in I.D. glass column packed with 10% FFAP was used in the analysis of the spiked samples. The results are presented on the following page.

Table S157-1

| Sorbent | Result |
|---|---|
| 100 mg Charcoal Lot 105 | Approximately 10% recovery |
| 150 mg Silica Gel, 20/40 mesh | Less than 5% recovery |
| 75 mg Chromosorb 103, 60/80 mesh | Partially dissolved |
| 75 mg Tenax GC, 35/60 mesh | Completely dissolved |
| 75 mg Porapak Q, 50/80 mesh | Partially dissolved |

Further work with Tenax GC indicated a desorption efficiency of 85-100% when acrylamide was desorbed with deionized water. A test of the pressure drop across a glass tube (7 cm long, 6-mm O.D. and 4-mm I.D.) containing 75 mg of 35/60 mesh Tenax GC in the front section and 37 mg in the back-up section gave the following results:

Table S157-2

| Flow | Pressure Drop |
|---|---|
| 1.5 liter/minute | 7.2 inches of Hg* (183 mm Hg) |
| 0.185 liter/minute | 10 inches of water (19 mm Hg) |
| 0.50 liter/minute | 2.4 inches of Hg (61 mm Hg) |

*The pressure drop was so great that it compacted the Tenax in the tube.

Although the pressure drop at 0.185 liter/minute flow rate is acceptable for the operation of a personal sampling pump, it would require a sampling period greater than 8 hours to obtain sufficient sample for analysis.

In order to analyze acrylamide by gc, which looked promising, collection of acrylamide in a midget impinger containing water was investigated. It was assumed that a very large sample volume of 672 liters at 2.8 liters per minute, containing both vapor and particulate acrylamide could be sampled with a midget impinger. Method recoveries at three levels (0.5X, 1X, and 2X the OSHA standard levels) were started. As a result of numerous injections during one day, the FFAP column previously described deteriorated; the peak shape was not adequate and the peak areas were no longer reproducible, especially at the 0.5X level. Subsequent FFAP columns exhibited the same deterioration within a few days of use. Deterioration may have been due to decomposition of the column packing with numerous injections of water solutions. The FFAP columns appeared to become darker in color with use, and occasionally a solid plug of column packing would form near the inlet of the column, thus blocking passage through the column. Attempts to find a column that would not deteriorate were made, without success. A list of columns that were tried is given in Table S157-3.

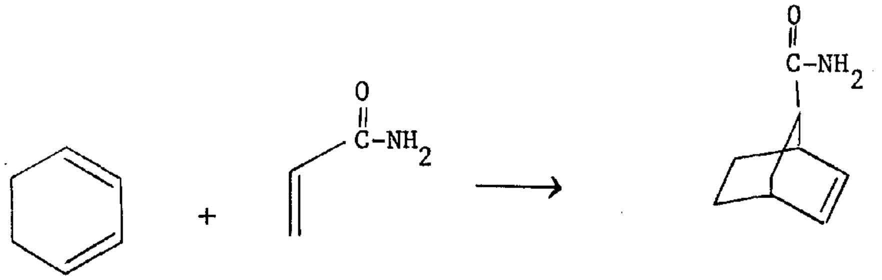
## Table S157-3

## Column Trials

| | |
|---|---|
| 6-ft x 1/4-in O.D. glass column packed with 5% OV-17 on Chrom W DCMS, 80/100 mesh | Even concentrated solutions of acrylamide gave broad tailing peaks. The 1X level could not be detected. |
| 4-ft x 1/4-in glass column packed with 10% FFAP with 1 ft of 5% OV-17 on Chrom W DCMS, 80/100 mesh at the inlet of the column | The peak was satisfactory at 5X the OSHA standard level, but at the 1X level, the peak was barely above the noise level and tailed badly. |
| 6-ft x 1/8-in O.D. stainless steel column packed with 10% FFAP with 1-1/2 ft of 5% OV-17 on Chrom W DCMS, 80/100 mesh at the inlet end of the column | The results were the same as the FFAP column above. Both columns took a long time to respond consistently to acrylamide in water solutions. |
| 4-ft x 1/8-in stainless steel column packed with Tenax GC, 60/80 mesh | The peak shape and sensitivity were inadequate. |
| 4-ft x 1/4-in stainless steel column packed with Chrom 102 | The peak shape and sensitivity were inadequate. |

Since increasing the size of the molecule prior to gc analysis should increase the gc sensitivity, two attempts were made to derivatize acrylamide.

The first method attempted was a Diels-Alder reaction of acrylamide with 1,3-cyclohexadiene.



1,3-Cyclohexadiene

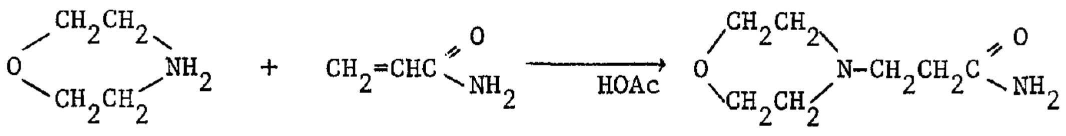
Cyclopentadiene was the reagent of first choice, but was not used due to its tendency toward polymerization.

Five milligrams of acrylamide was added to a 1:100 excess of cyclohexadiene in chloroform. Several solvents were tried; methanol and acetone caused immediate precipitation of what was believed to be a cyclohexadiene polymer. Chloroform dissolved both reactants and did not cause a precipitate of either reactants or products.

After 72 hours at ambient conditions, the solution was chromatographed on a 20% TCEP/Chromosorb W column, yielding peaks identifiable as unreacted cyclohexadiene and unreacted acrylamide (18 minutes). Several peaks eluted after the acrylamide, including a sizeable and distinct peak at 30 minutes, which was not identified but is believed to be a polymerization product.

A literature search yielded several papers on Diels-Alder reactions with acrylamide and 2-phenyl-1,3-butadiene (References 1 and 2). Vigorous conditions (reflux for 3 days) gave poor yields (45%); there were other indications of deactivation of the double bond in acrylamide due to the amide group. On the basis of the literature search and experimental results, this method was abandoned.

The second derivatization method attempted was a reaction with morpholine. According to Critchfield, et. al, (Reference 3) acrylamide reacts quantitatively with morpholine at room temperature in the presence of acetic acid catalyst as follows:



A reaction mixture was made with 2 ml morpholine, 1.5 g acrylamide, and 5 ml of 1:1 acetic acid in water. Several attempts were made to gas chromatograph aliquots of this mixture, but a peak attributable to the reaction product was not found. The columns tried were Tenax GC, 5% SE-30, Chromosorb 103, and 10% FFAP.

Another derivatization procedure discussed in the literature (Reference 4) consists of bromination of acrylamide, followed by gas chromatography of the $\alpha,\beta$-dibromopropionamide obtained, using an electron capture detector. This method appears to have adequate sensitivity, but it was not considered attractive for testing in this program because of the lengthy derivatization and extraction procedures and of the reported low yields of the brominated product (66% at an acrylamide concentration in water of 500 micrograms/liter.)

A differential pulse polarographic method (DPP) was suggested for determination of acrylamide. Reduction of the acrylamide occurs at about -2.0 v vs a standard calomel electrode (SCE) (Reference 5). In general, any electrochemical study more cathodic of -1.8 v is complicated by reduction of solvent or supporting electrolyte. In the above work, the acrylamide peak is superimposed on a solvent reduction tail. The referenced method used 1 N tetra-n-butylammonium hydroxide as supporting electrolyte. The solution was approximately 20% methanol. By conventional polarographic technique, 100 ppm acrylamide is immeasurably low. For a 1 ppm standard acrylamide solution using DPP, a total peak height of about 9.5 microamps was obtained, but 4 microamps of this was due to background and solvent tail. From this same work DPP measurement of standard acrylamide solutions in the range of 1-96 ppm yielded a CV of response factors ($i_{peak}$/conc.) of 0.054. The fact that "pure" samples analyzed in a research laboratory gave a CV this high, suggests that real collected samples analyzed in a routine analysis laboratory will not meet NIOSH criteria for precision and accuracy. Specificity is also lacking in this method in that some alkyl esters of acrylic acid and substituted acrylamides are indistinguishably reduced at the same potential (Reference 6).

A recent publication (Reference 6) describes an analytical procedure for the determination of trace levels of acrylamide in an aqueous solution using ion-exclusion liquid chromatography. A variable wavelength detector operated at 225 nm is necessary. The reported minimum detectable level is 25 ng in a 0.5 ml volume injected onto the column. Based on the assumption that 672 liters could be collected in 10 ml of water, 10 micrograms of acrylamide in a 0.5 ml volume would be injected onto the column. This is 400 times the amount reported as the minimum detectable level. The precision of the method at 160 times the minimum detectable level is 0.025 (Reference 6). Because of the lack of time, no work was done on this method. It should be noted, however, that the work in the publication was done by a research laboratory, and real samples which are analyzed in a routine analysis laboratory may not achieve the same precision.

Reference 7 gives a method of analysis for primary amides by means of flame emission spectrometry. In this method, barium hypobromite reacts with primary amides to form the amine of one less carbon and insoluble barium carbonate. Excess barium is removed, and the separated barium carbonate is dissolved in acid and determined by flame emission spectrometry. This method is not specific for acrylamide; it determines the total primary amide content of a sample. In order to make this method specific for acrylamide, it would be necessary to develop a method by which acrylamide could be separated from other primary amides. A sample size of about 500 micrograms was used in Reference 7, but a minimum detectable level was not given. This method may also be dependent on the ability to collect a sufficient amount of acrylamide.

## Recommendations

Data from the literature (Reference 8) indicate that acrylamide may be present in air as both vapor and particulate. The method must collect both vapor and particulate acrylamide. A collection in a midget impinger containing water at a flow rate of 2.8 liters/minute is recommended.

Analysis by ion-exclusion liquid chromatography as described in Reference 6 is recommended. It is amenable to collection in water and is reported to have adequate sensitivity and precision.

Alternately, additional effort could be expended to find suitable conditions for gas chromatographic analysis. Sensitivity might be obtained by use of a nitrogen-specific detector or a photoionization detector. The use of other column packing materials should be investigated. An effort should be made to either find a column packing that does not deteriorate when water is injected or alternately, to use an alcohol as the trapping medium (or desorbing solvent if a solid sorbent is used for collection of air samples.)

## References

1. Meek, John S., et al., "Diels-Alder Reactions of 2-Phenyl-1,3-butadiene," JACS, 73, 12, (Dec. 1951), 5563-5565.

2. Meek, John S., et al., "The Condensation of trans-1-Phenyl-1,3-butadiene with Acrylonitrile, Acrylyl Chloride, Acrylamide, and Propiolic Acid," JACS, 74, 10, (May 20, 1952), 2669-2672.

3. Critchfield, Frank, et al., "Determination of Alpha, Beta-Unsaturated Compounds by Reaction with Morpholine," Anal. Chem., 28, 1, (Jan. 1956), 76-79.

4. Croll, B. T. and G. M. Simkins, "The Determination of Acrylamide in Water by Using Electron-Capture Gas Chromatography," Analyst, 97, (April 1972), 281-288.

5. Betso, S. R. and J. D. McLean, "Determination of Acrylamide Monomer by Differential Pulse Polarography," Anal. Chem., 48, 10, (April 1976), 766-770.

6. Husser, E. R., et al., "Liquid Chromatographic Determination of Residual Acrylamide Monomer in Aqueous and Nonaqueous Dispersed Phase Polymeric Systems," Anal. Chem., 49, 1, (Jan. 1977), 154-158.

7. D'Alonzo, R., and S. Siggia, "Determination of Micromolar Quantities of Primary Amides by Flame Emission Spectrometry, Anal. Chem., 49, 2, (Feb. 1977), 262-265.

8. Carpenter, E. L. and H. S. Davis, "Acrylamide. Its Preparation and Properties," J. Applied Chem., 7, Dec. 1957.

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**15. Supplementary Notes**

NA

**16. Abstract (Limit: 200 words)**

Test results using the NIOSH analytical method S157 for acrylamide (79061) are reported. The technique involved collection on a solid sorbent or in a midget impinger containing water, desorption with organic solvents and water, derivatization with 1,3-cyclohexadiene or morpholine, and analysis with gas chromatography using a flame ionization detector. Data on recovery rates for charcoal, silica gel, chromosorb-103, Tenax-GC, and Porapak-Q sorbents is included. Solid sorbents were unsatisfactory because of large pressure decreases, and midget impinger collection was unsatisfactory because the chromatographic column was not sufficiently sensitive and would not withstand repeated injections. Derivatizations with 1,3-cyclohexadiene were incomplete after 24 hours, and the morpholine derivative could not be chromatographed.

**17. Document Analysis a. Descriptors**

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