Air Products and Chemicals INC.

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Date 8 November 1977

To J. D. Kramer

Subject ACETYLENICS PLANT INDUSTRIAL HYGIENE MONITORING PROGRAM

From R. J. Lomicky

cc: J. A. Allbritten
O. Culver
R. W. McGinnis
J. C. Novak/Trexlertown
M. H. Stermon
H. L. Watson/Trexlertown

As per the recent request to institute immediately a total Plant Industrial Hygiene Monitoring Program, the following is the proposed program to be followed at the Acetylenics production unit. The following program will list suggested locations to measure various utilized chemicals, the frequency and timing of sampling, and suggested forms to record information. The Acetylenics Plant will also institute its own Leak Detection Program to monitor organic concentrations around the various process equipment and tankage. The use of a Century Vapor Analyzer, borrowed from PVOH, will be utilized for this program. The total Leak Detection Program will be better defined at a later date.

It is suggested that we initially use a hand-held portable gas sampling detector pump utilized with Gastec Detector Tubes to get base line data on the more commonly used plant chemicals such as acetone, MEK, IPE, acetylene, etc. The air sampling pump and stain tubes can detect the threshold limit values of various chemicals in the plant operating areas to permit more definitive air sampling to begin utilizing the carbon absorbing sampling pumps. Shown on the attached sketches and data forms are the various suggested locations to obtain initial air test samples using stain tubes. It is requested that we immediately begin weekly air testing using the stain detector tubes to provide initial base line data. Following initial stain tube results, weekly sampling, utilizing the carbon absorption air detectors, can be instituted to measure Isopropyl Ether and various carbonyls as various products are manufactured.

Continued sampling in the KOH operation area should be completed twice weekly using the Bendix pumps with midget impingers of 1.8 liters/minute to measure for total caustic dust. See attached measurement data sheet for recommended sampling points in the caustic building.

Immediate implementation of dust measurements at the product flaker operation should also be instituted. Daily sampling during flaker operation should be utilized with the Bendix pumps at 2 liters/minute to measure total dust. The Acetylenics Plant will advise the hygiene monitoring personnel of the days and times when the flaker is in operation during DO and DH flaking.

SUBJECT: ACETYLENICS PLANT INDUSTRIAL HYGIENE MONITORING PROGRAM

A review of recent Acetylenics Plant Industrial Hygiene Program monitoring reveals that only KOH dust samples around the caustic building flaker have been measured and obtained. It is imperative that DO and DH product flaker dust measurements and organic concentrations in the operating areas be monitored immediately. The Acetylenics Plant supervisors will work closely with Roy McGinnis and Buddy Stermon to assure collection of the required samples at the recommended weekly frequency. Once the data is accumulated and analyzed, it will be utilized as part of the monthly Acetylenics Plant report.

Shown attached are five (5) sketches detailing the plant tank farm areas, outside process area, and inside process area. On each sketch suggested sampling locations for air monitoring of organic chemicals have been selected. Also attached are data sheets detailing other suggested sampling locations for both organic chemicals and dust measurements. Results obtained from the air sampling can be recorded directly on the attached data sheets for the various sampling locations.

Also included is the list of commonly utilized organic chemicals at the Acetylenics Plant, along with established T.L.V.'s. Where applicable, stain tube measurements should be initially obtained to determine where exposure problems exist. Then carbon absorption samples can be obtained on a weekly sampling frequency.

If there are any comments or questions, please advise. Everyone's cooperation is appreciated.

R. J. LOMICKY

RJL/bc

ACETYLENICS PLANT

WEATHER CONDITIONS (General Description)

DATE: 28 Nov 77

Cold, Dry, Wind from N @ 5 mph

TIME: ~ 1000

ESTABLISHED T.L.V. _____

DETECTOR INSTRUMENT Dräger Tubes 100-12,000 ppm CHEMICAL MEASURED C=O (Ketones)

LOCATION	TUBE READING CONCENTRATION (%)	TUBE READING CONCENTRATION (PPM)	TEMP. C°	TEMP. CORRECTED CONCENTRATION (%)	TEMP. CORRECTED CONCENTRATION (PPM)	REMARKS
TANK FARM AREA #1		None Detected	3	None required	ND	
TANK FARM AREA #2		<100	3	0-40°C	<100	
TANK FARM AREA #3		<100	3		<100	
TANK FARM AREA #4		<100	3		<100	
BALL MILL BLDG.						
WASH WATER & PHASE SEPARATOR AREA						
OUTSIDE PROCESS AREA #1		<100	3		<100	
UTSIDE PROCESS AREA #2		<100	3		<100	
INSIDE PROCESS AREA #1		<100	8		<100	
INSIDE PROCESS AREA #2		~100	8		~100	
INSIDE PROCESS AREA #3		<100	8		<100	
INSIDE PROCESS AREA #4		~100	8		~100	
SECOND FLOOR PRODUCT STILL						
THIRD FLOOR PRODUCT STILL						

COMMENTS: _____

ACETYLENICS PLANT ORGANIC MEASUREMENTS

WEATHER CONDITIONS (General Description)

DATE: _____

TIME: _____

DETECTOR INSTRUMENT Air Pump Sampler/Carbon

OPERATOR NAME: _____ CHEMICAL MEASURED _____

LOCATION	TIME START	TIME END	TOTAL TIME	TEST RESULTS	REMARKS
TANK FARM AREA #1					
TANK FARM AREA #2					
TANK FARM AREA #3					
TANK FARM AREA #4					
BALL MILL BUILDING					
WASH WATER & PHASE SEPARATOR AREA					
OUTSIDE PROCESS AREA #1					
OUTSIDE PROCESS AREA #2					
INSIDE PROCESS AREA #1					
INSIDE PROCESS AREA #2					
INSIDE PROCESS AREA #3					
INSIDE PROCESS AREA #4					
SECOND FLOOR PRODUCT STILL					
THIRD FLOOR PRODUCT STILL					

COMMENTS: _____

ACETYLENICS PLANT DUST MEASUREMENTS

WEATHER CONDITIONS (General Description) _____

DATE: _____

TIME: _____

DETECTOR INSTRUMENT Air Pump Sampler/Dust

OPERATOR NAME: _____ CHEMICAL MEASURED _____

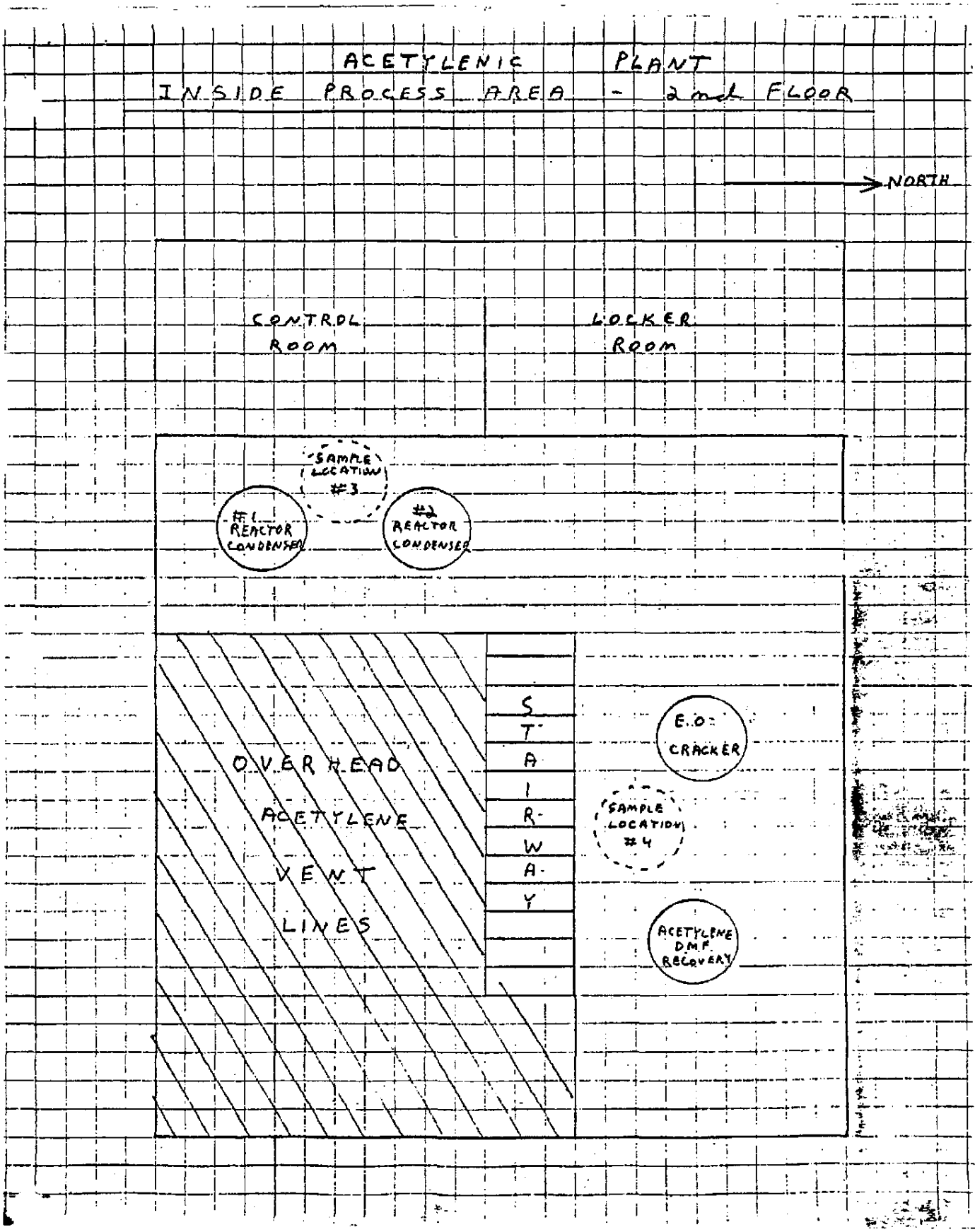
LOCATION	TIME START	TIME END	TOTAL TIME	TEST RESULTS	REMARKS
FIRST FLOOR CAUSTIC BLDG. AT DELTAINER CHUTE					
SECOND FLOOR CAUSTIC BLDG. AT BALL MILL					
SECOND FLOOR CAUSTIC BLDG. AT EAST POT					
SECOND FLOOR CAUSTIC BLDG. AT WEST POT					
FIRST FLOOR AT BALL MILL GATE					
SECOND FLOOR BALL MILL ROOM					
PRODUCT FLAKER ROOM AT DRUM					
PRODUCT FLAKER ROOM AT NORTH END					

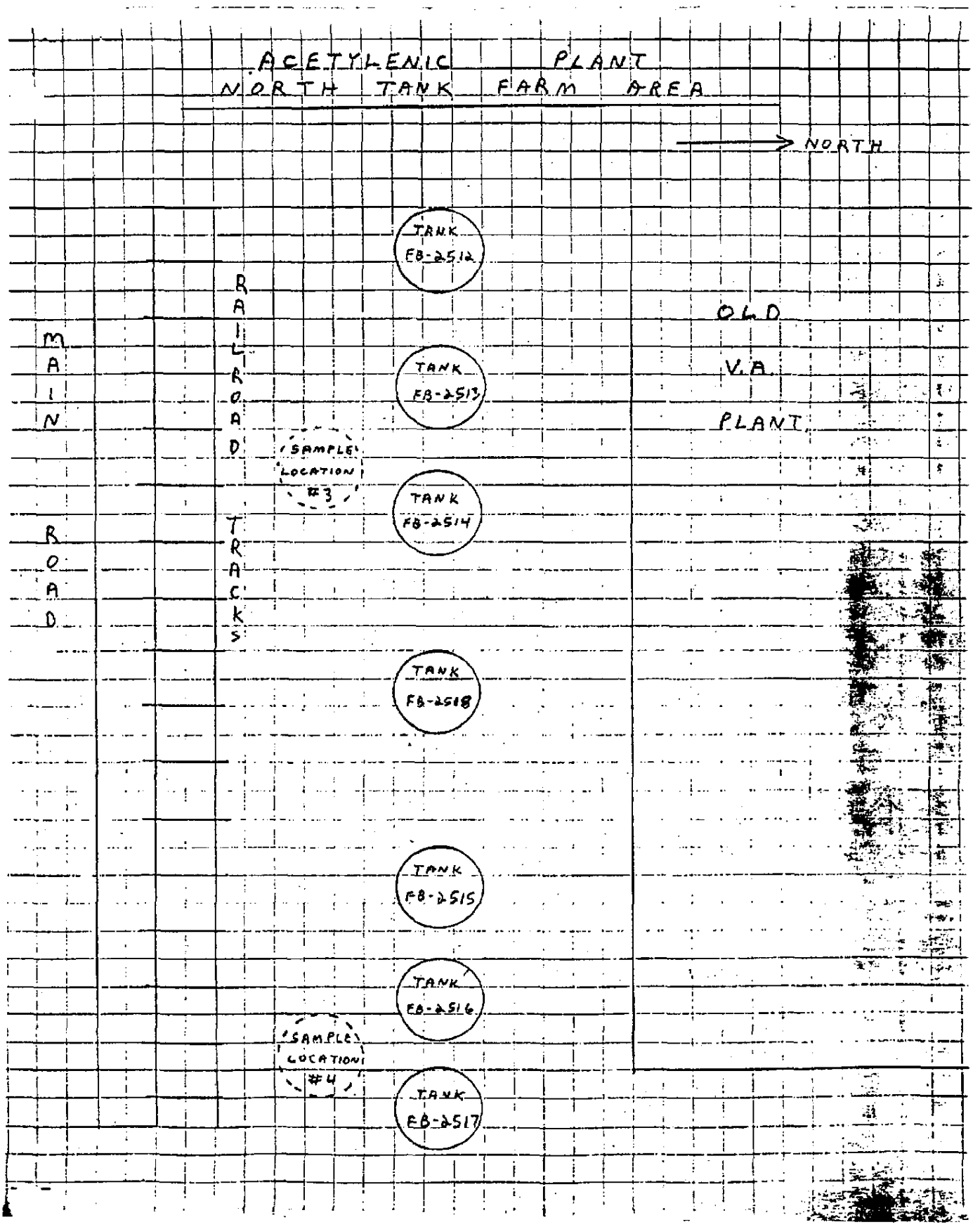
COMMENTS: _____

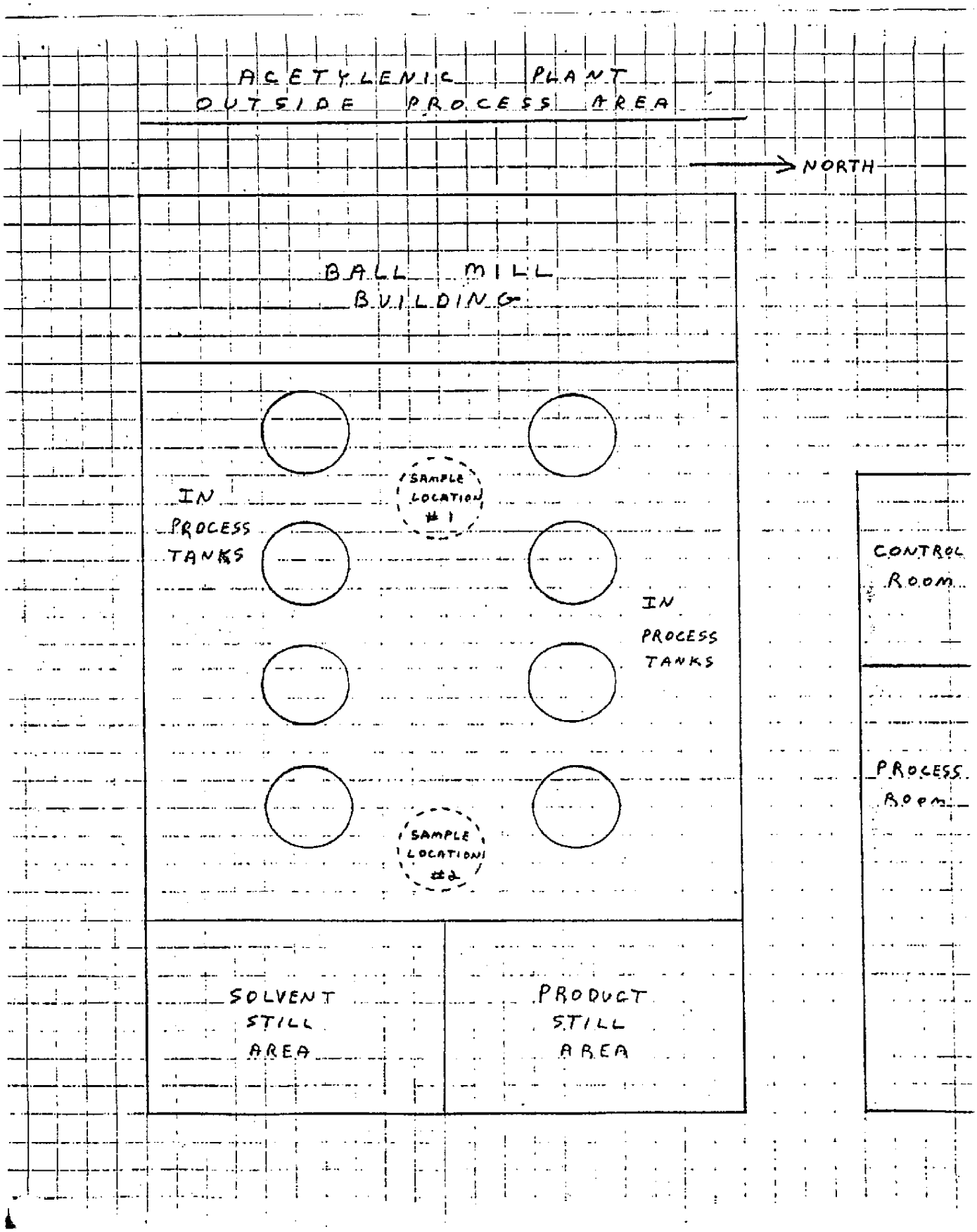
1 x 1000 =

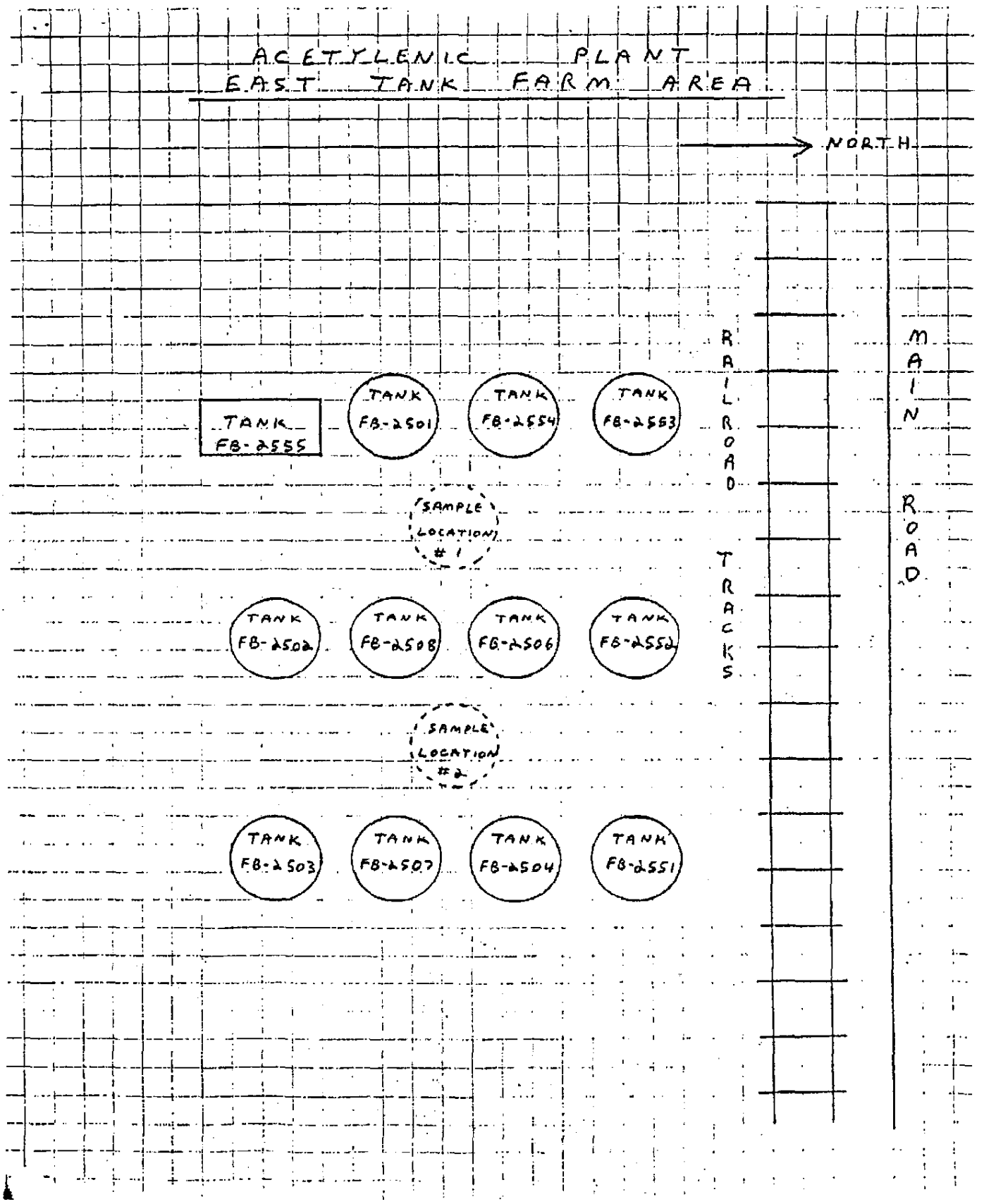
AP00043675

ACETYLENIC PLANT
INSIDE PROCESS AREA - 2nd FLOOR




ACETYLENIC PLANT
NORTH TANK FARM AREA
NORTH
TANK FB-2512
TANK FB-2513
TANK FB-2514
TANK FB-2518
TANK FB-2515
TANK FB-2516
TANK FB-2517
SAMPLE LOCATION #3
SAMPLE LOCATION #4
MAIN ROAD
RAILROAD TRACKS
OLD V.A. PLANT


ACETYLENIC PLANT
OUTSIDE PROCESS AREA
NORTH
BALL MILL
BUILDING
IN
PROCESS
TANKS
SAMPLE
LOCATION
#1
IN
PROCESS
TANKS
CONTROL
ROOM
PROCESS
ROOM
SAMPLE
LOCATION
#2
SOLVENT
STILL
AREA
PRODUCT
STILL
AREA


ACETYLENIC PLANT
EAST TANK FARM AREA
NORTH
TANK FB-2555
TANK FB-2501
TANK FB-2554
TANK FB-2553
SAMPLE LOCATION #1
TANK FB-2502
TANK FB-2508
TANK FB-2506
TANK FB-2552
SAMPLE LOCATION #2
TANK FB-2503
TANK FB-2507
TANK FB-2504
TANK FB-2551
RAILROAD TRACKS
MAIN ROAD

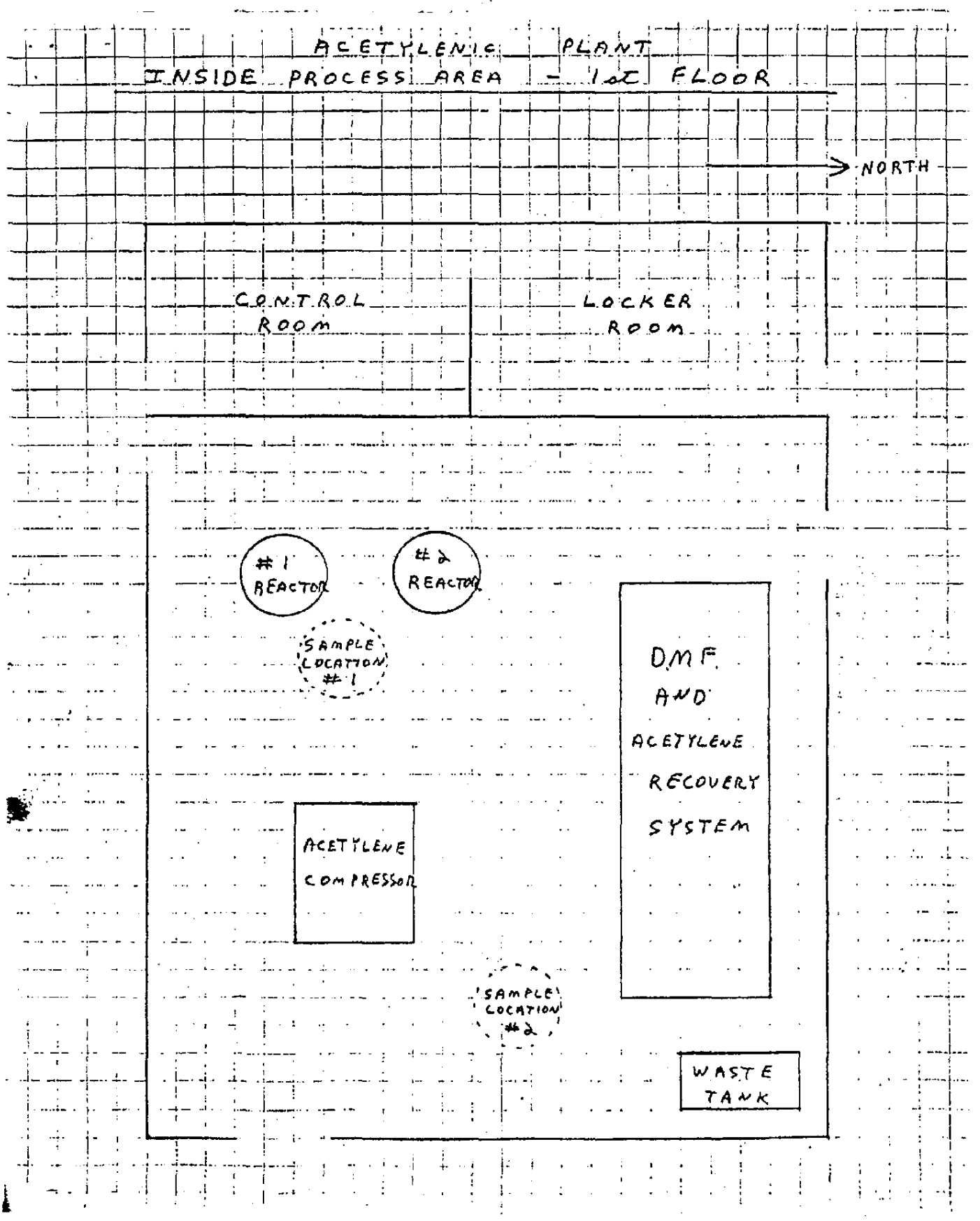

ACETYLENIC PLANT
INSIDE PROCESS AREA - 1st FLOOR
NORTH
CONTROL ROOM
LOCKER ROOM
#1 REACTOR
#2 REACTOR
SAMPLE LOCATION #1
DMF AND ACETYLENE RECOVERY SYSTEM
ACETYLENE COMPRESSOR
SAMPLE LOCATION #2
WASTE TANK

TABLE I

ACETYLENICS PLANT PROCESS CHEMICALS

CODE	CHEMICAL	ESTABLISHED T.L.V.	SAMPLING FREQUENCY	STAIN TUBE AVAIL.
1304-101	Acetylene	Asphix.	Weekly	Yes
-102	Acetone	1000	During DH/ MB Run	Yes
-104	Butraldehyde	Not Est.	During OW-1 Run	No
-107	Isopropyl Ether	250	Weekly	No
-108	Ethyl Hexaldehyde	Not Est.	During EO Run	No
-109	2-Ethyl Hexanol	Not Est.	S-104 Blend	No
-111	Igepal AT-548	Not Est.	S-104 Blend	No
-112	KOH - 90%	2	Weekly	No
-113	Methyl Ethyl Ketone	200	During MP/ DO Run	Yes
-114	Methyl Isobutyl Ketone	100	During S-104 Run	Yes
-116	PolyGlycol 2000	Not Est.	S-104 Blend	No
-117	Propargyl Alcohol	1	EO Blending	No
-118	Renex 20	Not Est.	S-104 Blend	No
-132	Ethylene Glycol	100	S-104 Blend	No
-183	Propylene Glycol	100	S-104 Blend	No
-	DiMethyl Formamide	10	Weekly	Yes

A technique has been developed to validate gas and vapor sampling methods under field insult conditions. Laboratory validation, a necessary aspect of good laboratory practices, only tests the feasibility of a sampling method. *"Field validation"* determines the effectiveness of a given sampling method in the actual workplace environment where potentially interfering components may exist. A simple and inexpensive means is shown for introducing a known addition spike onto the sampling device during sampling. The validation sample is subject to the same field conditions as area or personnel samples. Upon analysis, recovery of the known addition spike within specified limits, verifies validity of the day's samples. Insufficient known addition spike recovery alerts the hygienist that something has caused sample failure, resulting in an invalid measurement of worker exposure.

Validation of gas and vapor sampling methods under field insult conditions

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Introduction

Currently promulgated regulations are forcing industry to test the validity of sampling and analytical techniques used in industrial hygiene monitoring. Section E6 of the Emergency Temporary Standard for acrylonitrile, and the OSHA field directive no. 300, made evident that methods must be validated in order to be in compliance. Prior to 1979, NIOSH published procedures[1] used laboratory generated data for a *"one component"* analyte system to validate their methods. Plant environments may well have multiple gas and vapor components which must be considered. These components may vary qualitatively and quantitatively from day to day, and indeed from moment to moment. Depending on adjacent processes and wind direction, one could have multiple sampling interferences one day and none the next day. These two sampling situations are quite different from each other and obviously much different from earlier NIOSH laboratory generated sampling protocols. Temperature and humidity are other factors that have been shown to adversely affect the performance of sampling devices. Field validation reveals the existence of these problems by testing the reference working curve on a daily basis.

Field validation will not reveal specific causes of sampling method failure, but will indicate when failure occurs. By validating an area sample in the same general area that personnel samples are taken, one may assume all samples in that area can be considered valid. To implement this program, one needs a device to introduce a vapor spike onto the sample tube and an adept person to spike the tube.

We believe that this procedure far exceeds OSHA monitoring method requirements. If worker exposure is to be determined, both sampling and analytical validity must be ensured. This technique begins to tie together the integrity of both the sampling and the analytical procedures. Chain of custody from the field through the laboratory process can be assured using field validation.

validation equipment

To implement field validation one needs a means to introduce a vapor spike. A glass gas bulb fitted with a suitable septum works well. We recommend that the internal volume of the gas bulb and the flow rate allow at least 10 volume changes per hour. To calculate the maximum internal volume necessary for a long duration sample, i.e. greater than 4 hours, do the following:

$$\text{volume of bulb (cc)} = \frac{\text{flow rate used in sampling (cc/min.)} \times 60 \text{ min./hr.}}{10 \text{ air volume changes/hr.}}$$

Smaller internal volumes may be used affording increased transfer rates. This becomes necessary when validating sampling procedures for short term exposure level (STEL) monitoring. All other validation equipment is identical to that required in the sampling method.

procedure

developing a calibration curve

Standard solutions of analyte in the range equivalent to expected levels in the workplace air must first be prepared. Recommended levels are 0.2x, 0.5x, 1x, 2x, and 5x the permissible exposure level (PEL). The NIOSH solvent flush technique[2] is strongly recommended for all syringe injections. We also recommend a minimum of 6 injections per concentration in order to obtain good statistical data. These individual concentration responses are then averaged. Average *instrument* response vs. μg in the standard $\pm$ 2 standard deviations ($\pm 2\sigma$) data are determined at each point. Figure 1 illustrates a calibration curve which is used in conjunction with the reference working curve used for field validation.

A daily test of the calibration curve should fall within $\pm 2\sigma$ at any point. Failure to do so requires regeneration of the curve.

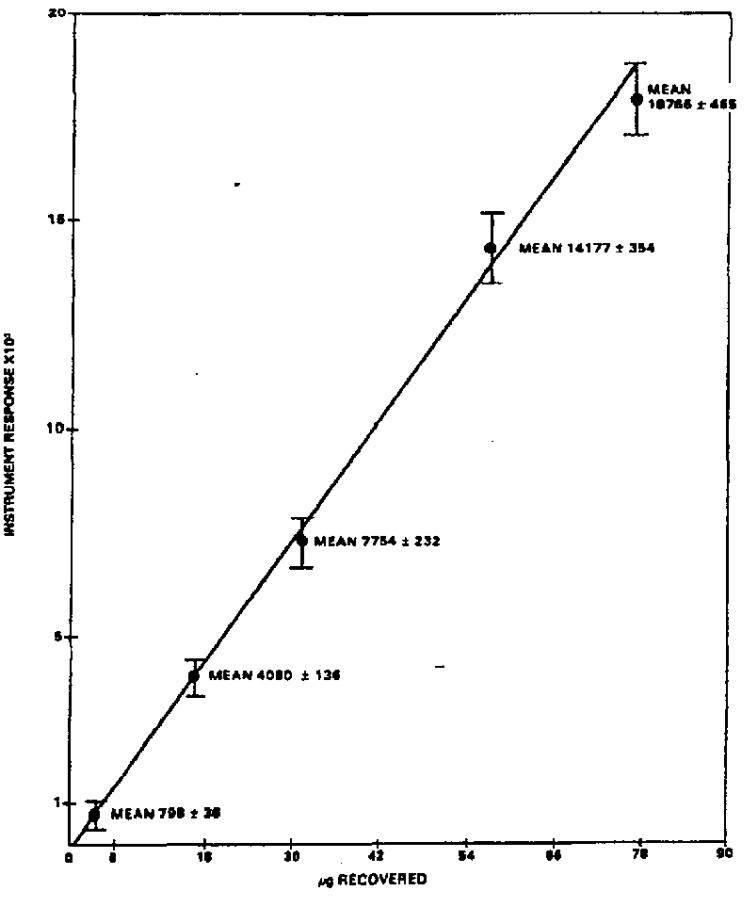

Figure 1 — Calibration curve for Benzene.

developing a reference working curve

This curve is generated by vapor spiking a sampling device using the gas sampling bulb and then analyzing to determine μg recovered.[3] In developing the working curve, it is important to set the air flow at the level that actual sampling is performed (±10%) because the working curve can vary as a function of flow rate. Repetitive runs are made to enable means and standard deviations to be calculated. The analytical "*μg recovered*" is obtained from the calibration curve, Figure 1. The "*μg actual*" is the known addition spike. These values are plotted to generate a reference working curve in Figure 2, not desorption efficiency as advocated by NIOSH. NIOSH protocol states that a method fails when the desorption efficiency is less than 75%. The working curve allows an extension of the linearity at lower limits and an improved coefficient of variation at the 95% confidence level (CV_T) with no compromise of data quality. For example, the data for acrylonitrile sampling generated by OSHA[4] using a modified NIOSH procedure[5] utilizing desorption efficiency was replotted on a reference working curve. By using the reference working curve approach, the method showed a linear response to exposures of an order of magnitude lower than the approach used by OSHA, while exceeding the actual performance of the method required by the OSHA acrylonitrile standard.[6]

field validation

Assemble 2 sample trains as in Figure 3. Calibrate the flow with a loosely packed charcoal tube between the soap film flow meter and the sampling device. It is extremely important to keep both sample train inlets as close to one another as possible when sampling.

After 25% of the total sampling time has elapsed, the bulb is spiked with an aliquot of standard. It is essential to wait before spiking, because the sample tube should be exposed to the environmental matrices before the validation test begins. In practical application field validation is a means of determining whether the sampling and analytical integrity have been maintained. Therefore the sampling device must be exposed to the environment before the known addition spike is added. This should reveal whether the analyte remains adsorbed or whether it is lost due to matrix conditions. The spike recovered should be 100% ± 25% of theoretical. If the validation is not within these limits, then something in the environment interfered with the method causing it to fail.

field data

Table I contains field validation data obtained while sampling for acrylonitrile.[7] The data shown are averages of

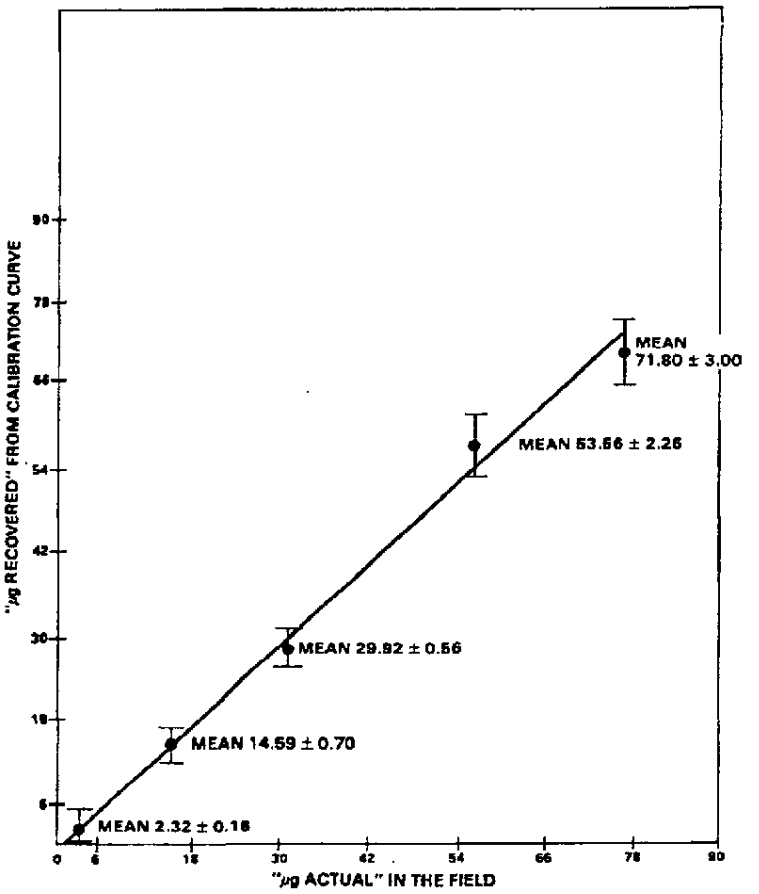

Figure 2 — Reference working curve for Benzene.

several sampling and analytical determinations. All samples were obtained in the same operating unit utilizing an identical sampling and analytical procedure. Using the ±25% criteria, field samples taken during field validation trial 2 are considered valid. The reason for failure in trials one and three is not known; but the unit in which the samples were taken is subject to local high humidity conditions on a random basis. The industrial hygienist was able to better interpret the exposure data because of the use of field validation. A new sampling strategy to avoid high humidity operations was adopted based on this data.

discussion

limitations of this technique

Since the field validation procedures require the use of a glass bulb, it is not recommended for actual personnel samples. This limits the use of this procedure to area samples only. However, if several people work in a non-transient area, a validated area sample under the day's worst environmental conditions would in principle validate all samples taken in that area. We recommend field validation be done on a daily basis because random day-to-day environmental changes have been observed as the cause of method failure as illustrated in the field data shown in Table I.

Field validation will apply only when the analyte is completely vaporized. Heating the glass bulb may become necessary to obtain complete vaporization and mass transfer of some compounds. Maleic anhydride is an example of such a compound.

Once calibration and reference working curves have been developed, they become good indices of method problems.

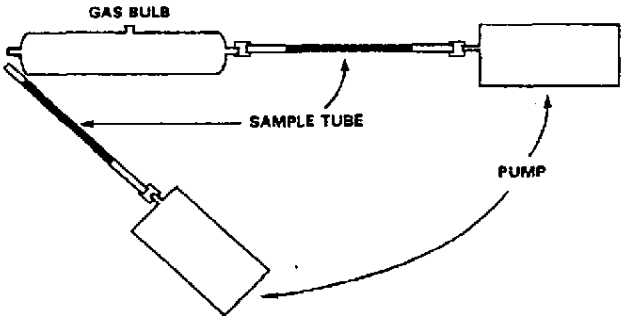

Figure 3 — Sample train for field validation.

TABLE I
Field Validation Data

Sample	Ambient Environ. Conditions	Background Control*	Field Spike	Background plus Spike*	Spike Found*	Spike Recovered (avg.)
no. 1	Jan., 1978 Temp. 21 °C	12.0 μg	8.0 μg	22.5 μg	10.5 μg	131% (invalid)
no. 2	July, 1978 Temp. 30 °C	44.0 μg	16.0 μg	62.1 μg	18.1 μg	113% (valid)
no. 3†	July, 1978 Temp. 30 °C	10.0 μg	8.0 μg	14.8 μg	4.1 μg	51% (invalid)

*All values are "μg actual" obtained from the reference working curve.

† This sample had a steam unit operating in the near vicinity.

All samples are 20L volume with charcoal lot no. 106 obtained from SKC, Inc., R.D. 1, no. 395 Valley View Road, Eighty Four, PA 15330.

For example, problems with the sampling device are detected through the reference working curve and problems with the analytical device are detected through the calibration curve.

Field validation is not the answer to all the sampling problems we encounter. Field validation will not reveal the specific causes of method failure, but it will indicate when failure occurs. This becomes very important if exposure is to be accurately determined and evaluated. Monitoring data without appropriate validation can be dangerously misleading. *"False negatives"* may cause an area of concern to be overlooked, while *"false positives"* may cause unnecessary and expensive corrective procedures to be implemented. Performing field validation of vapor and gas samples avoids such errors and assures the quality a defensibility of monitoring data.

references

1. U.S. Dept. of Health, Education and Welfare: *NIOS Manual of Analytical Methods*. 2nd Ed. Vol 1, 2, 3 (197
2. U.S. Dept. of Health, Education, and Welfare: *NIOS Manual of Analytical Methods*. 2nd Ed. Vol. 2, S19, (197
3. Deitrich, M.W., L.M. Chapman and J.P. Mieure: Sa pling for Organic Chemicals in Workplace Atmospher with Porous Polymer Beads. *Am. Ind. Hyg. Assoc. J. 39*:38 392 (1978).
4. Exhibit 18A, OSHA Acrylonitrile Hearing, March, 1978.
5. Federal Register, *43*:45818-45819, October 3, 1978.
6. Federal Register, *43*:45810, October 3, 1978.
7. Sheridan, D.L.: Monsanto intercompany communiq between D.L. Sheridan and P.M. Jeannot. (1979).

Joint Occupational Health Conference

The Joint Occupational Health Conference, sponsored by the American Academy of Occupational Medicine and th American Academy of Industrial Hygiene, will be held at the Hyatt Regency Hotel in San Francisco, CA, October 28 31, 1980. This year, for the first time, the Society of Toxicology is also a participant. For a copy of the program an registration forms write or call the American Academy of Industrial Hygiene, 475 Wolf Ledges Parkway, Akron, OI 44311 (216) 762-7707.