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## I. Summary

On May 1, 1987, the National Institute for Occupational Safety and Health (NIOSH) received a request from representatives of the Technical Services Division, U.S. Department of the Treasury, Bureau of Engraving and Printing, to provide technical assistance with an evaluation program undertaken to assess contaminants released from inks supplied by currency ink contract bidders. Specifically, the bureau requested our assistance in four areas: (1) confirmation of NIOSH's ability and willingness to assist the bureau with their effort to evaluate contaminants, and specifically irritant compounds falling into the general grouping of aldehydes, released by the inks during the currency production process; (2) to provide confirmation that (a) the bureau's assumption that aldehydes are a plausible cause of reported irritant effects among workers and that (b) the bureau's test protocol to evaluate the inks as a source of aldehyde emissions is likely to provide useful emission data; (3) to conduct a site visit to observe the bureau's study and verify that the study is being conducted as proposed; and (4) to provide an expert specializing in aldehyde analyses to evaluate all aspects of the testing procedure including sample preparation, standard preparation, instrument conditions and parameters, data acquisition and reduction, and the conclusions reached from the analyses.

NIOSH investigators responded to this request by conducting an initial survey addressing the analytical and evaluation protocol concerns of the bureau June 17-18, 1987. Independent work conducted by NIOSH investigators during a follow-up industrial hygiene survey August 18-21, 1987, allowed evaluation of worker exposures to contaminants associated with examining currency and also permitted confirmation of suspected contaminant identities on air samples collected in the work areas of concern. The specific process of concern was U.S. currency inspection.

Personal exposure and area sampling was conducted for acetaldehyde, acrolein, formaldehyde, butanal, pentanal, and hexanal. Area sampling was conducted at selected work stations for solvent vapors-both qualitatively and quantitatively. Exposures associated with regular currency production and two test currencies were evaluated.

Formaldehyde area concentrations ranged from 0.13 to 0.25 mg/m$^3$ (0.1 to 0.2 ppm). Personal exposure values for formaldehyde fell below the analytical limit of detection which approximated an exposure level below 0.3 to 0.7 mg/m$^3$ (0.3 to 0.6 ppm). NIOSH recommends that formaldehyde exposures be maintained at the lowest feasible level. The OSHA Permissible Exposure Limit (PEL) is 1.2 mg/m$^3$ (1 ppm). Butanal concentrations, both personal exposure and area, ranged from N.D. to 1.4 mg/m$^3$ (0.5 ppm). The only occupational exposure criteria for butanal identified is a Russian Maximum Allowable Concentration (MAC) of 5 mg/m$^3$ (1.7 ppm). Pentanal exposures ranged from were present in trace amounts, less than 0.72 mg/m$^3$ (0.2 ppm). The ACGIH TLV for pentanal is 175 mg/m$^3$ (50 ppm). Hexanal levels were present in trace amounts, less than about 1.0 mg/m$^3$ (0.2 ppm). No occupational exposure limits were identified for hexanal. Personal exposures and area airborne concentrations of acetaldehyde and acrolein were nondetectable (N.D.). Area solvent vapor concentrations for acetone, 1,1,1-trichloroethane, and toluene were negligible (N.D. or trace). Mineral spirits and kerosene values ranged from N.D. to 63 mg/m$^3$ and trace to 12 mg/m$^3$ respectively, well below the NIOSH RELs of 350 mg/m$^3$ for mineral spirits and 100 mg/m$^3$ for kerosene.

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Based upon the NIOSH industrial hygiene survey results, irritant health effects associated with exposures to formaldehyde encountered during currency examination potentially exist. Exposures to acetaldehyde, acrolein, butanal, pentanal, and hexanal were sufficiently low that they are not considered likely to represent an appreciable potential health hazard. Exposures to solvent vapors of acetone, 1,1,1-trichloroethane, toluene, mineral spirits, and kerosene were equally low, unlikely to constitute a significant health hazard. Recommendations offered in Section VIII of this report addressed modifications to the study protocol and analytical method used by the bureau in evaluating aldehydes offgassing from the currency inks, local exhaust ventilation, and a to search for a substitute for formaldehyde containing resins in the currency paper.

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KEYWORDS: SIC 2754 (Commercial Printing, Gravure) 9311 (Public Finance, Taxation, and Monetary Policy) currency production, acetaldehyde, acrolein, formaldehyde, butanal, pentanal, hexanal, currency examination.

## II. INTRODUCTION

On May 1, 1987 the National Institute for Occupational Safety and Health (NIOSH) received a request from representatives of the Technical Services Division, U.S. Department of the Treasury, Bureau of Engraving and Printing, to provide technical assistance with an evaluation program undertaken to assess contaminants released from inks supplied by currency ink contract bidders. The bureau was interested in not only selecting inks that were best suited for use as a currency ink, but also presented the least amount of health risk to the currency production workers. Specifically the bureau requested four assistance actions from NIOSH. These were: (1) confirmation of NIOSH's ability and willingness to assist the bureau with their effort to evaluate contaminants, and specifically irritant compounds falling into the general grouping of aldehydes, released by the inks during the currency production process; (2) to provide confirmation that (a) the bureau's assumption that aldehydes are a plausible cause of reported irritant effects among workers and that b) the bureau's test protocol to evaluate the inks as a source of aldehyde emissions is likely to provide useful emission data; (3) to conduct a site visit to observe the bureau's study and verify that the study is being conducted as proposed; and (4) to provide an expert specializing in aldehyde analyses to evaluate all aspects of the testing procedure including sample preparation, standard preparation, instrument conditions and parameters, data acquistion and reduction, and the conclusions reached from the analyses. Survey summary letters were sent to the bureau on July 7, 1987, and on September 1, 1987.

## III. BACKGROUND

### A. Basis of the Bureau of Engraving and Printing's Request:

An increase in worker reports of health effects associated with handling currency, especially during the examination process, elevated Bureau management concerns that contaminant emissions of an irritant nature associated with handling the currency may present a health hazard to bureau workers. Incidents of workers reporting to the employee health unit had increased in frequency since October 1986. A number of the incidents coincided with evaluating currency printed with test inks supplied by ink manufacturers bidding on a multimillion dollar contract to provide currency inks for a one year period starting in November 1987. These episodes, however, were not exclusively limited to the test currency evaluation process. Some of these episodes were associated with regular currency production.

The number of workers (reportedly) affected in any one incident ranged from one to 10 workers. This number includes only those workers reporting to the employee health unit with complaints. Health effects reported by the workers included headaches; nausea; burning eyes, nose, and throat; dizziness; and an "uncomfortable feeling". Some workers also reported elevations in blood pressure, however inquiry of the nursing supervisor in charge of the health unit revealed that a number of the workers seen were under treatment for hypertension. Almost all of the incidents occurred during the day shift. Workers reporting symptoms were both male and female and many reportedly associated their symptoms with the ink on the currency. Some individuals were involved in more than one incident. As a result of these incidents and the previously stated concerns, the bureau set out to evaluate the potential health risks associated with handling currency printed with inks supplied by the various ink contract bidders.

### B. NIOSH Activities:

#### 1. Initial Survey:

In response to the bureau's request NIOSH investigators conducted an initial site visit June 17 and 18, 1987, to provide assistance as technical advisors on the various evaluation efforts being undertaken by the Division of Technical Services associated with the currency ink procurement process. During this survey the request was further defined and included: assessment of the sampling and analytical procedures used in evaluating contaminants offgassing from printed notes using current production inks; identification and confirmation of contaminants from ink offgassing that may result in potential worker exposures during currency production; and suggestions along with possible assistance regarding the protocol development and conduct of exposure monitoring during currency ink test runs. A request for assistance with the analysis of samples collected by the bureau was also put forth, requiring exploration of how and to what extent such services could be offered as well as the feasibility of responding to this additional request.

The NIOSH investigators met with the various representatives involved with the currency ink evaluation process, the analytical chemist assigned to the project, the Safety Manager, and the Nursing Supervisor of the Employee Health Unit. Discussions included further definition of the request; activities conducted by the bureau to date; review of the analytical work performed by the Division of Technical Services laboratory on this project to date; inquiry concerning past industrial hygiene assessments regarding contaminants present in the press and examining rooms; obtaining summary information about exposure incidents associated with irritants released during currency production; and a walk-through tour of the process and production areas. The NIOSH chemist conducted a review of the information and procedures used by the bureau in addition to evaluating their study protocol devised to address irritant contaminants released from the contract bidders' currency inks. Activities of this survey were summarized and submitted to bureau representatives July 7, 1987.

Subsequent to the initial survey, an interagency agreement was established between NIOSH and the Bureau of Engraving and Printing to allow for the analysis of samples generated by the bureau during their study evaluating test currency ink emissions. Additional guidance concerning the study protocol was provided by the NIOSH investigators. Assistance concerning the industrial hygiene assessment of worker exposures during the mechanical examination of the test currency was also requested by the Bureau in addition to providing the bureau with a suggested sampling protocol, a limited industrial hygiene survey was conducted by NIOSH in a follow-up survey.

2. Industrial Hygiene Follow-up Survey:

The follow-up industrial hygiene survey was conducted August 18 to 21, 1987, and consisted of two days of personal exposure and area sampling for contaminants released during mechanical examination of the currency. Personal exposure monitoring was conducted for acrolein and a number of aldehydes identified as offgassing from the currency. The specific aldehydes were: formaldehyde, acetaldehyde, butanal, pentanal, and hexanal. Propanal and heptanal, although known to be potentially present, were not being evaluated because of limitations with the analytical method. Area sampling conducted at the mechanical examination stations included additional samples for solvents.

The NIOSH follow-up survey duplicated personal and area sampling being conducted on test loads of currency by the bureau's industrial hygiene contractor. This involved side-by-side sampling of the A1 and A3 face examiners' exposures to aldehydes; duplication of the three area samples for aldehydes and acrolein; and charcoal tube samples for other organic compounds that may be released from the inks.

Exposure monitoring of workers at two mechanical examining stations inspecting regular production currency involved sampling all four examiners and the bookbinder for aldehyde exposures, and the A3 face examiner for acrolein. A set of area samples for aldehydes, acrolein, and solvents was also collected at the A3 face examination work station. A total of 27 full-shift personal exposure samples for aldehydes was obtained. This included both regular and test production over the two day survey.

C. Bureau Test Currency Sampling Findings and Past Industrial Hygiene Data:

Industrial hygiene sampling conducted by the bureau's safety department coinciding with the occurrence of incidents of irritant health effects associated with currency handling addressed formaldehyde, acrolein, and acetaldehyde. Concentrations for acrolein and acetaldehyde were generally negligible and those for formaldehyde were all less than 1.2 milligrams per meter cubed of air ($mg/m^3$) (1 part per million (ppm)). Reported formaldehyde concentrations ranged from 0.12 $mg/m^3$ (0.10 ppm) to 0.37 $mg/m^3$ (0.30 ppm). No written reports of the sampling data were available for review by the NIOSH investigators.

Contaminants evaluated by the bureau's Division of Technical Services involved sampling for gaseous contaminants inside of sealed plastic bags or steel boxes containing the various test currencies printed with the different bidders' inks. The results demonstrated the present of large amounts of butanal, pentanal, and hexanal (milligrams per sample). Formaldehyde, acetaldehyde, and heptanal were also present in lesser amounts in some or all of the samples, depending upon the type of substrate (paper) printed upon and the presence or absence of any or all ink (green or black). This data prompted the subsequent sampling of environmental levels to evaluate airborne contamination resulting from the different currency inks. Note that confirmation of compound identity had not been specifically performed other than for its concurrence with the standards of the identified aldehydes.

### D. Process Description and Suspected Contaminant Sources:

The Bureau of Engraving and Printing is responsible for production of all United States currency. The printing of the currency involves single pass intaglio printing. The notes are printed on a special currency paper which contains a melamine formaldehyde resin to impart wet strength to the finished product. Two inks are used, black and green, with green applied first and then after about a 48 hour curing period the black or face is applied. The inks cure by oxidative polymerization.

The exact formulations of the inks are unknown to the bureau, however a review of the material safety data sheets (MSDS) supplied by the four ink manufacturers responding to the ink contract solicitation revealed little information regarding hazardous ink constituents. Three of the four manufacturers state that irritation of the eyes, skin, and of respiratory passages may occur from exposure to the inks. The fourth manufacturer states that no health effects are anticipated with exposure occurring during the normal use of their product. This last manufacturer tended to provide more information on the product MSDS concerning specific constituents that may present a health hazard. The inks are composed of three primary parts: the vehicle containing resins and solvents; the color which contains metal pigments or oxides; and ink driers (metal soaps) which may contain cobalt, lead, or manganese compounds-for example lead octoate. None of the aldehydes identified by the bureau are listed as an ink constituent by any of the ink manufacturers.

Loads of currency are brought into the mechanical examination areas from vaults after a 24 to 48 hour holding period after printing has been completed. The loads, two stacks of 10,000-32 subject sheets, are opened by the bookbinder, separated on a vibrating table, and shingled out onto the currency feeder as needed to maintain a continuous flow of the sheets through the mechanical examining unit and past the examiners. During this process the sheets are cut and trimmed to two 16 subject sheets and defective sheets are pulled out by the bookbinder and examiners. The examining units have four examiners who examine the face (front) and backs of the currency sheets. Regular production currency examination ranges from 35 to 40 thousand 32 subject sheets per work shift. It is during this process that most of the health effects have occurred among the workers. This is the first opportunity for separation of the individual sheets after the currency has been printed.

The loads are locked down tightly during storage and must be broken apart by the bookbinder after removal of the locking strap. Odors are often reported when the loads are opened up and the quality and intensity of the odors reportedly varies even within a load, such as between the two 10,000 sheet stacks of currency that constitute a single press run (load).

At the time of the survey no emission controls were present on the mechanical examining units for removal of vapors coming off of the currency. Ink dust was observed to accumulate along the sides of the feeder. Electrostatic precipitators were mounted from the ceiling in the mechanical examining areas above the units, however their effectiveness could not be determined for particulate released into the room, and these units were totally ineffective against odors or vapors released from the currency. The temperature and relative humidity was closely regulated in both the printing and mechanical examining areas. Temperatures were maintained around 72 to 74 Farenheit and the relative humidity was held between 45 and 55%.

## IV. EVALUATION METHODS AND MATERIALS

### A. Initial Survey:

This part of the survey involved a review of the bureau's activities to address contaminants released from the test inks. This included discussions between the NIOSH chemist and the bureau chemist assigned to the project, inspection of the data generated to date and evaluation of the methods used for the sampling and analysis of contaminants released by the inks. The industrial hygiene evaluation involved a walk-through of the process and interviews with the Safety Manager and the nursing supervisor of the Employee Health Unit. Although discussed verbally, no written industrial hygiene reports addressing past contaminant sampling in the examining areas were made available for review. Information concerning the incidents involving worker health complaints was similarly presented in a generalized verbal discussion.

## B. Follow-up Industrial Hygiene Survey:

The follow-up industrial hygiene survey involved personal and area sampling for contaminants released during the mechanical examining process of both regular production and test currency. Contaminants evaluated were: acrolein; aldehydes identified by the bureau-formaldehyde, acetaldehyde, butanal, pentanal, and hexanal; a set of samples for an aldehyde screen to identify and confirm the presence of suspected aldehydes; and samples to permit identification of solvent vapors present followed by quantitation of compounds selected from the qualitative samples. Sample duration approximated the full work shift.

## C. Sampling and Analytical Methods:

### 1. Acrolein:

Acrolein samples were collected using ORBO-23* sorbent tubes and a sampling air flow rate of 50 cubic centimeters per minute (cc/min). The front and back sections were separated and analyzed by gas chromatography (GC) using NIOSH Method 2501(1) with modifications. The modifications were:

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| Desorption: | 30 minutes with sonication in 2.0 milliters of toluene. |
| Gas Chromatograph: | Hewlett-Packard Model 5711A equipped with a nitrogen-phosphorus detector. |
| Column: | 6' x 1/4" glass (2 millimeter internal diameter (mm i.d.) packed with 5% SP-2401 DB on 100/120 Supelcoport. |

Oven Conditions: Temperature programmed from 90° Centigrade (C) to 190°C at a rate of 32°C/minute.

Standards were spiked on ORBO-23* tubes submitted by the NIOSH industrial hygienist and desorbed the same as the samples. The limit of detection (LOD) was 2 micrograms (ug)/sample for acrolein and the limit of quantitation (LOQ) was 6 ug/sample.

### 2. Formaldehyde, Acetaldehyde, Butanal, Pentanal, and Hexanal:

Samples were collected on ORBO-22* sorbent tubes using a sampling flow rate of 50 cc/min. The front and back sections were separated and analyzed by GC using the method supplied to NIOSH by the Bureau of Engraving and Printing, Appendix A.

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| Desorption Process: | One hour minimum (after 20 minutes sonication) in 1.7 milliters (mL) of toluene containing 0.25 microliter per mL of n-hexadecane as an internal standard. |
| Gas Chormatograph: | Hewlett-Packard Model 5711A equipped with a flame ionization detector (FID). |
| Column: | 30 meter (m) x 0.315 mm fused silica capillary column coated internally with a 0.25 micrometer thick film (um) of Durawax DX-4. |

Oven Conditions: Thermal programming 110°C to 220°C at 8°C/min.

Standards for formaldehyde were spiked onto the A section (front) of Supelco ORBO-22* tubes and desorbed the same as the samples. Standards for the rest of the aldehydes were spiked into 1.7 mL of toluene containing the A section of Supelco ORBO-22* tubes and were desorbed the same as the samples. The analyst reported that the peak for formaldehyde was extended both in the standards and Datachem quality control samples. At the end of the analytical run, a high level spike of propanal on the ORBO-22* tube was desorbed and analyzed. The propanal peak eluted very closely with the formaldehyde peak, and therefore was considered an interference.

The LOD and the LOQ for the analytes were: formaldehyde-LOD 8 ug/sample, LOQ-25 ug/sample; acetaldehyde-LOD 6 ug/sample, LOQ-20 ug/sample; butanal-LOD 5 ug/sample, LOQ-17 ug/sample; pentanal-LOD 5 ug/sample, LOQ-17 ug/sample; and hexanal-LOD 7ug/sample, LOQ-21 ug/sample.

3. Screening and Confirmation of the Various Airborne Aldehydes Present in Mechanical Examining:

   Aldehyde screening samples were collected on ORBO-23* sorbent tubes at a sampling flow rate of 50 cc/min. The samples were desorbed with 1 mL of toluene in an ultrasonic bath for 60 minutes. Samples were screened by gas chromatography (equipped with a FID) using a 30m DB-WAX capillary column (splitless mode). Representative samples were then analyzed by gas chromatography-mass selective detector (GC-MSD) to identify compounds. Samples were quantitated for formaldehyde using spiked tubes for standards. The LOD for formaldehyde was about 0.4 ug/sample and the LOQ was about 1.5 ug/sample.

4. Qualitative and Quantitative Sampling for Solvent Vapors:

   Standard SKC charcoal tubes were used for area sampling evaluating solvent vapors present at the mechanical examiners' work stations. A sampling rate of 50 cc/minute was used and samples were generally collected in pairs, allowing one for one analysis characterizing the airborne contaminants present and a second for quantitating selected compounds identified in the first analysis.

   a. Qualitative Analysis:

      All charcoal tube samples were desorbed with 1 mL of carbon disulfide and initially screened by gas chromatography (FID) using a 30-meter DB-1 fused silica capillary column (splitless mode). Representative samples of the charcoal tube samples were then analyzed by GC-MSD to identify components.

      Samples that had been collected by the bureau on ORBO-32* charcoal tubes were analyzed in this same fashion, with the front and back sections analyzed separately. Estimates of the total amount of hydrocarbons present on these samples (those collected by the bureau) were determined using a mineral spirits bulk for the standards.

   b. Quantitative Analysis:

      The front sections of the charcoal tube air samples were transferred to serological vials and treated with carbon disulfide for a minimum time period of thirty minutes with occasional agitation. Aliquots were then injected into a Hewlett-Packard Model 5890 gas chromatograph equipped with a 30-meter SPB-1 fused silica capillary column. A flame ionization detector was used to detect compounds eluting from the column.

      Quantitation was accomplished by comparing analyte peak areas of the samples with those of prepared standards. The hydrocarbon peaks were quantitated in terms of mineral spirits and kerosene by using laboratory materials for this purpose. The results should be considered as estimates since the chromatographic patterns of the laboratory materials and field samples were similar but not identical.

      The analytical LODs and LOQs in mg/sample for the selected analytes follow: Acetone-LOD 0.01, LOQ 0.03; 1,1,1-trichloroethane-LOD 0.01, LOQ 0.03; Toluene-LOD 0.04, LOQ 0.13; Mineral spirits-LOD 0.02, LOQ 0.07; and Kerosene-LOD 0.02, LOQ 0.07.

## V. EVALUATION CRITERIA AND TOXICOLOGY DISCUSSION

### A. Environmental Criteria

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (REL's), (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs), and (3) the U.S. Department of Labor (OSHA) occupational health standards. Often, the NIOSH REL's and ACGIH TLVs are lower than the corresponding OSHA standards. Both NIOSH REL's and ACGIH TLVs usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH REL's, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

### B. Toxicology Discussion:

Irritancy is a property of nearly all of the aldehydes, however it occurs more commonly and is more important in the case of those with lower molecular weights and those with unsaturation in the aliphatic chain. Direct sensitization to aldehyde vapors appears to be relatively rare. Sensitization to the unsaturated aldehydes may occur, but it is usually difficult to separate primary irritation from sensitization. Direct evidence of the human effects of aldehydes is related predominantly to eye irritation, odor threshold, and irritation of the upper respiratory tract and skin. To a lesser degree, isolated human biochemical reactions have been monitored. In general, the higher the molecular weight of the aldehyde, the more saturated the aliphatic chain of the aldehyde, and the absence of halogenated substitutents on the carbon chain, the less the irritant properties of the aldehyde are.(5) The following paragraphs will present a brief toxicology discussion of the aldehydes evaluated during this health hazard evaluation.

#### 1. Acetaldehyde:

Acetaldehyde is an irritant of the eyes and mucous membranes. The irritant effects of the vapor at lower concentrations, such as cough and burning sensation in the nose, throat, and eyes usually prevent exposure sufficient to cause central nervous system depression.(6) Acetaldehyde is less irritating to the human eye, nose, and throat than formaldehyde and acrolein. It has a vasopressor effect, i.e., it increases blood pressure, in common with other aliphatic aldehydes. Marked increases in blood pressure have not been observed in test animals until an acetaldehyde exposure concentration at or above 2,990 mg/m$^3$ of air or 1,665 ppm is attained. The lowest toxic concentration ($TC_{LO}$) for an observed health effect in humans is 240 mg/m$^3$ (134 ppm). The carcinogenic potential of acetaldehyde has not been defined by long-term animal studies.(5) The OSHA permissible exposure limit (PEL) for an eight hour time weighted average (TWA) is 360 mg/m$^3$ (200 ppm).(4) The ACGIH TLV* of 180 mg/m$^3$ (100 ppm) is intended to prevent excessive eye irritation and potential injury to the respiratory tract.(7)

2. Acrolein:

   Acrolein is a severe eye and respiratory system irritant. The principle site of chemical effects is the mucous membranes of the upper respiratory tract. Acrolein is toxic by all routes of administration. It has not been shown to be carcinogenic or embryotoxic. Acrolein has a vasopressor effect which has been observed in animals (rats) at exposure levels of 10 to 5029 mg/m$^3$ (4.4 to 2200 ppm) for one minute. The unsaturated nature of the compound results in an eye irritancy potential 2.5 times greater than that of formaldehyde. At higher acrolein concentrations (1.1 to 2.3 mg/m$^3$ (0.5 to 1.0 ppm)) the irritant potential increases to four or five times that of formaldehyde at the same concentrations. The $TC_{LO}$ for human responses to acrolein are 0.5 mg/m$^3$ (0.2 ppm)-eye irritation threshold; and 1.4 mg/m$^3$ (0.6 ppm)-respiratory response threshold. The human odor threshold is 0.75 to 0.9 mg/m$^3$ (0.33 to 0.4 ppm). Acrolein is a major contributor to the irritant properties of cigarette smoke.(5) The OSHA PEL for acrolein is a TWA of 0.25 mg/m$^3$ (0.1 ppm).(4) The ACGIH TLV* of 0.25 mg/m$^3$ (0.1 ppm) is considered sufficiently low to minimize, but not entirely prevent, irritation among all exposed individuals.(7)

3. Butanal:

   Irritation of the eyes and upper respiratory tract has been caused by exposures to butanal. Human exposures of 677 mg/m$^3$ (230 ppm) for a period of 10 minutes have been reported as non-irritating.(5) No OSHA PEL, ACGIH TLV, or NIOSH REL have been identified for butanal. The USSR has a Maximum Allowable Concentration (MAC) of 5 mg/m$^3$.(8)

4. Formaldehyde:

   Formaldehyde gas is an irritant of the eyes and respiratory tract; solutions cause both primary irritation and sensitization dermatitis.(6) The first signs or symptoms noticed upon exposure to formaldehyde at concentrations ranging from 0.1 to 6 mg/m$^3$ (0.1 to 5 ppm) are burning of the eyes, tearing (lacrimation), and general irritation of the upper respiratory passages. Higher exposures (12 to 25 mg/m$^3$ (10 to 20 ppm)) may produce coughing, tightening in the chest, a sense of pressure in the head, and palpitation of the heart. NIOSH developed a REL in 1976 for formaldehyde of 1.2 mg/m$^3$ (1 ppm) to prevent the irritant effects of exposures to this compound.(9) This recommendation predated the development of animal carcinogenicity data implicating formaldehyde as an animal carcinogen and a potential occupational carcinogen. Formaldehyde has also produced positive results in mutagenicity testing, supporting the classification of this compound as a potential occupational carcinogen. NIOSH currently considers formaldehyde a human carcinogen and recommends that formaldehyde exposures be maintained at the lowest feasible level.(10,11)

   On December 4, 1987, OSHA promulgated a new health standard for formaldehyde, which becomes effective on February 2, 1988.(12) In the standard OSHA considers formaldehyde a probable human carcinogen. The PEL was reduced by two thirds, from 3.6 mg/M$^3$ (3 ppm) to 1.2 mg/M$^3$ (1 ppm), as an 8-hour TWA. Exposures up to 7.2 mg/M$^3$ (2 ppm) would be permitted for 15 minute periods as long as the daily exposure does not exceed 1.2 mg/M$^3$. The revised standard contains provisions for medical surveillance, record keeping, regulated areas, emergency procedures, control strategies, protective equipment, and hazard communication. Some of these provisions, however, may not be required of employers until after the effective date.

   The ACGIH TLV* for formaldehyde is 1.5 mg/m$^3$ (1 ppm) but also classifies formaldehyde as a suspected human carcinogen necessitating that exposures be kept to a minimum.(3)

5. Hexanal:

Hexanal or n-hexaldehyde has a sharp aldehyde odor.(13) Mild skin and eye irritation have been observed in rats exposed via inhalation to hexanal. Carcinogenicity, mutagenicity, and teratogenicity have not been determined for hexanal.(5) No occupational exposure criteria for hexanal are listed in the OSHA general industry standards(4) or by NIOSH or ACGIH.

6. Pentanal:

Human exposure data is not available concerning responses to differing levels of pentanal. Chemists engaged in the distillation of isovaleraldehyde (a structural isomer of n-valeraldeyde or pentanal) developed chest discomfort, nausea, emesis (vomiting), and headaches. The odor was reported to be very pronounced during this incident and the concentration may have been high.(5) The ACGIH TLV* for pentanal, listed as n-valeraldehyde, is 175 mg/m$^3$ (50 ppm). This limit is intended to prevent irritation of the skin and eyes associated with pentanal exposures. Further industrial experience with the handling of this compound is needed to evaluate the suitability of this TLV*.(7) No OSHA PEL currently exists for pentanal, nor is there a NIOSH REL for this compound.

## VI. INITIAL SURVEY FINDINGS AND FOLLOW-UP SURVEY SAMPLING RESULTS

### A. Initial Survey Findings and Observations:

The Technical Services Division has been engaged in evaluating ink samples supplied by manufacturers bidding on a one year contract to supply currency inks, beginning in November 1987. Part of this evaluation involved air sampling of contaminants released by the inks and printed notes utilizing the various manufacturers' inks. Comparison of these results to the results obtained under the same type of conditions from current production inks had been undertaken in a systematic manner. Sampling has consisted of test samples obtained in closed plastic bags over a consecutive number of days following various stages of the printing process. Several controls were also included in an effort to isolate contaminant sources. The analytical work to date has focused on a number of irritant compounds, specifically a series of aliphatic aldehydes and acrolein.

Concern regarding the release of contaminants into the work areas during the production processes, particularly mechanical examination, has increased during the past year. Several incidents of acute irritation associated with inspecting and handling recently printed notes, both during regular production and with test inks, have been attributed to the aldehydes observed to be coming from the notes in the test samples.

Workplace monitoring for aldehydes, specifically formaldehyde and acrolein, has been conducted when complaints were reported. No air sampling has been attempted in the production areas for the other aldehydes identified from the laboratory samples. These other aldehydes, as mentioned previously, include acetaldehyde, butanal, pentanal, hexanal, and heptanal. Reported formaldehyde concentrations associated with worker complaints in the mechanical examining areas ranged from 0.1 to 0.4 mg/m$^3$ (0.05 to 0.28 ppm). Documented acrolein levels in the vaults were between 0.5 to 1.4 mg/m$^3$ (0.22 to 0.55 ppm). Additional exhaust ventilation take-offs had been recently installed in the vaults to remove materials released by the notes during curing. These vents were located approximately six feet above the floor, and above the stacks of currency.

### B. Follow-up Industrial Hygiene Sampling Results:

In this section, qualitative analytical results for charcoal tube samples collected by the bureau using their test currency evaluation scheme will be presented briefly, followed by the quantitative sampling results obtained for personal exposure and area samples collected during the NIOSH follow-up industrial hygiene survey.

1. Qualitative Charcoal Tube Sample Results for Bureau Submitted Samples:

The twelve charcoal tube samples collected in the closed chambers by the bureau all had fairly similar chromatograms. Proportions varied, but the same major components were detected on all tubes. Four of the front sections and two of the backup sections of the sample tubes were analyzed by GC-MSD to identify or confirm the components. Butanal, pentanal, hexanal, and heptanal were present on all samples at various levels. Other major compounds identified were toluene, acetone, $C_{10}$-$C_{12}$ branched alkanes and n-alkanes in the $C_4$-$C_{16}$ range. All backup sections contained some acetone and lighter alkanes ($C_4$-$C_5$) and breakthrough (sample loss) for these compounds was probable.

Estimates for total hydrocarbon amounts found on these samples were determined using a mineral spirits ($C_9$-$C_{12}$) bulk for standards and by comparing the total area of the standards to the total areas of the sample peaks (sum of all peak areas within the chromatogram). These results are reported in Table I. Total areas for only the $C_4$-$C_7$ aldehyde peaks varied from sample to sample. The total aldehyde peak for sample C413, however, was from three to 10 times higher than any other sample. This sample was from the test ink evaluated environmentally August 19, 1987. The reconstructed ion chromatograms for samples C413 (front and back sections), C433 (the test ink evaluated environmentally August 20,1987), and C354-regular production ink (front and back sorbent tube sections) are presented as Figures 1 through 5 respectively.

2. Acetaldehyde, Acrolein, Butanal, Formaldehyde, Hexanal, and Pentanal Results:

   Table II presents the personal exposure and area sampling results for butanal, formaldehyde, hexanal, and pentanal. All samples for acetaldehyde and acrolein were below calculated environmental detection limits, less than 0.1 and 0.5 mg/m$^3$ (0.06 and 0.2 ppm) respectively. Calculated environmental limits of detection are obtained by dividing the LOD by the smallest sample volume collected presenting no detectable analyte. The same technique is used to obtain values for trace contaminant concentrations.

   Butanal concentrations, both personal exposure and area, ranged from below detection limits up to 1.4 mg/m$^3$ (0.5 ppm) with an arithmetic mean value of 0.73 mg/m$^3$ (0.2 ppm).

   Formaldehyde levels, for both personal and area samples, ranged from below detectable levels (89% or 32 of 36 samples) to trace amounts (11% or 4 of 36). The analytical LOD for the formaldehyde analyses of 8 ug/sample resulted in calculated environmental limits of detection of between 0.32 and 0.67 mg/m$^3$ (0.3 to 0.6 ppm), levels above those associated with primary irritant symptoms.

   Pentanal concentrations were present primarily in trace amounts or less than about 0.72 mg/m$^3$ (0.2 ppm).

   Hexanal concentrations were also present in trace amounts, less than about 1.0 mg/m$^3$ (0.2 ppm). Table II also has this data broken out by regular currency production and test currency production. Except for formaldehyde, none of the other aldehydes evaluated were considered to be at levels that could potentially be associated with irritant symptoms.

3. Qualitative Aldehyde Screen and Formaldehyde Quantitation:

   Area samples collected at each of the mechanical examination stations were analyzed for the various aldehydes identified by the bureau and then confirmed by mass spectroscopy. Aldehydes were detected on all of the area samples collected. Formaldehyde levels ranged from three to six micrograms per tube, 0.13 to 0.25 mg/m$^3$ (0.1 to 0.2 ppm), and are presented in Table III.

   Two of the samples were analyzed by GC-MSD to identify the derivative peaks. Figure 6 presents the reconstructed total ion chromatogram from the sample collected at the A3 face examining station of machine 972 on August 19, 1987. The presence of formaldehyde, propionaldehyde, butanal, pentanal, and hexanal was confirmed on all of the qualitative area samples. No acrolein was detected and the acetaldehyde derivative peak was too small for any positive confirmation by GC-MSD under these conditions. Based on comparison of peak heights between samples and spiked tubes containing butanal and pentanal, concentrations of $C_3$-$C_6$ aldehydes (propionaldehyde, butanal, pentanal, and hexanal) were estimated to be in the 5-20 ug per sample range.

4. Qualitative Area Sample Results for Solvent Vapors:

   The chromatograms for all area samples were similar to sample number 75, collected at the A3 face examining station of machine 978 on August 20, 1987, thus only this sample was analyzed by GC-MSD to identify components present. Figure 7 presents a copy of the representative reconstructed total ion chromatogram for these samples. Major compounds detected were toluene and various aliphatic hydrocarbons in the $C_9$-$C_{16}$ range, similar to mineral spirits ($C_9$-$C_{12}$) and kerosene ($C_9$-$C_{16}$). Other compounds identified included acetone, isopropanol, methylene chloride, 1,1,1-trichloroethane and xylenes.

5. Quantitation of Selected Solvents from Paired Area Samples:

1,1,1-trichloroethane was not detected on any of the area samples collected. Acetone and toluene levels were very low (trace amounts or N.D.). Airborne levels of mineral spirits and kerosene were also very low, even taking into consideration that concentrations for these two contaminants had to be approximated since bulk samples of the mineral spirits and kerosene used in the inks were unavailable. Table III presents the levels of solvent vapors by area sample location.

Methylene chloride, originally suspected to be present in minute quantities based upon the qualitative area sample results, could not be separated from the extraction solvent used in analyzing the samples. Attempts to resolve separation problems on two different chromatographic columns, SPB-1 and SPB-35, did not resolve the problem suggesting that this compound, if present, was below measurable quantities.

## VII. DISCUSSION AND CONCLUSIONS

### A. Comments Regarding the Bureau's Test Sample Protocol and Analyses:

The sampling and analytical work that has been completed to date on materials in current use by the bureau provides baseline data for evaluation of the test inks; however, recommendations are listed in the next section which will assist the bureau to more adequately fulfill the mission of currency ink evaluation. These recommendations were supplied to the bureau following the initial NIOSH survey.

The experimental design used for the evaluation of material offgassing did not make efficient use of the data collected. The bureau was encouraged to collect replicate samples in each of the test currency sampling chambers and reduce the total number of days during which sampling takes place, e.g. reduce sampling to days one (1), three (3) and seven (7) or whatever intervals are more reflective of actual conditions which the currency is subjected to during and after printing rather than collecting samples every day. Averaging of these sample results will allow a 95% confidence interval to be calculated for each set of replicates. The reason for this recommendation is that the 95% confidence interval for data is interpreted in some legal circles as proof beyond reasonable doubt.

The major concern with the modifications of the method used by the bureau for the collection of the aldehydes was breakthrough of the aldehydes onto the backup sections of the tubes. Observation of the data has indicated that breakthrough has happened only with acetaldehyde (ca. 10% of the samples) and formaldehyde (ca. 40% of the samples), and this breakthrough information is included by the bureau in their reports.

### B. Industrial Hygiene Discussion:

Comments made during the initial survey concerned modifications of exhaust ventilation installed in the currency vaults. No other specific discussion or recommendations were developed at that point in the HHE.

The personal exposure and area sampling conducted during the follow-up survey did not identify any specific health hazards associated with the examination of currency with the possible exception of formaldehyde. Atmospheric concentrations during the time frame of the NIOSH industrial hygiene survey revealed contaminant levels for acetaldehyde, butanal, pentanal, and hexanal well below (less than 1/10th to less than 1/100th) those levels identified in test currency samples collected by the bureau.

During the survey, measured exposures to the lower molecular weight aldehydes-acetaldehyde and acrolein-were negligible. The absence of acrolein and acetaldehyde in the personal and area samples was confirmed by qualitative analytical work coupled with compound identity confirmation on area samples obtained at each of the mechanical examining stations where sampling was conducted.

Formaldehyde concentrations were for the most part below the analytical limits of detection for the sampling and analytical method used for personal exposure sampling. The calculated environmental limit of detection for formaldehyde ranged from 0.32 to 0.67 mg/m$^3$ (0.3 to 0.6 ppm). This would be above environmental levels where individuals may begin to experience burning of the eyes, lacrimation, and general irritation of the respiratory passages. Paired area samples collected for aldehydes and analyzed qualitatively for formaldehyde, propionaldehyde, butanal, pentanal, and hexanal were also analyzed quantitatively for formaldehyde by a different method. This second analyses on different samples allowed quantitation of formaldehyde concentrations of 0.13 to 0.25 mg/m$^3$ (0.1 to 0.2 ppm) in the mechanical examining area. The presence of formaldehyde at these levels may be responsible for many of the irritant symptoms experienced by the workers.

The source of the formaldehyde is most likely due to the presence of a melamine formaldehyde resin used in the currency paper. The work conducted by the bureau concerning aldehyde levels associated with the various test currency samples demonstrated little variation in formaldehyde concentrations among regular production currency, test currency printed with the test inks, blind embossed currency paper (no ink but run through the press), and unprocessed blank currency paper.

Low level exposures, generally above detection limits but below quantifiable concentrations, to butanal, pentanal, and hexanal were documented for almost all personal and area samples involving regular currency production. This same observation is generally applicable to the sampling involving test currency. The occurrence of nondetectable levels of butanal, pentanal, and hexanal in the test currency personal exposure samples may be partly due to the smaller sample size associated with the shorter time periods during which the test currency loads were examined. The measured levels of these compounds do not represent a health hazard, based upon a comparison of the observed levels with toxicity information available for the specific compounds. (See Section V. Toxicology Discussion)

Area concentrations of acetone, 1,1,1-trichloroethane, toluene, mineral spirits, and kerosene were all well below the respective contaminants' evaluation criteria.

In summary, exposure levels of most airborne contaminants associated with examining currency did not present a health hazard to the workers in the mechanical examining area during the survey. The exception to this is the presence of formaldehyde at a range that has been reported to cause irritant symptoms in some individuals. Concerns regarding the potential carcinogenicity of formaldehyde should prompt efforts to reduce or eliminate exposures to this compound. The bureau has developed a baseline of information concerning the evaluation of test inks and appears to be moving toward further defining performance and contaminant emission criteria applicable to future inks used in currency production. The contaminant considered most likely to contribute to the reported irritant health effects appears from the results of this investigation to be formaldehyde.

## VIII. RECOMMENDATIONS

### A. Recommendations Addressing the Evaluation of Test Ink Samples:

1. Sampling pumps should be calibrated both before and after sampling, to ensure that the pump flow rate has not changed during sampling. This calibration should be performed with representative sampling media present in the sorbent tube holders.

2. The sample tubes should be positioned in the sample containers so that they are vertical. This can be done by placing a block under the sampling tubes to prop them up or byclipping them to the bracket located along the inside of the steel sampling chambers.

3. Two sample media blanks and two field media blanks should be analyzed along with every ten (10) collected samples. This helps eliminate problems if the media values vary, since an average media blank value can be reported and used to correct the sample data. Field media blanks are used to determine if sample contamination has occurred after sampling or during the sample workup or analytical procedures.

4. The number of analytical standards used for the preparation of the calibration curve should be increased from the three (3) standards currently used to at least five (5) or six (6), with each standard analyzed in triplicate. These standards should bracket the range of the sample values. Standards should be prepared at levels which will not overload the capacity of the analytical column. Samples may have to be diluted to prevent column overloading.

5. Quality control (QC) samples should be analyzed with each sample set. The amount of analyte present on the sample should be unknown to the analyst until the QC samples have been analyzed and results reported. Subsequent to the receipt of the QC results, a decision should then be made as to whether the analyses were in control and valid. This recommendation will require the assignment of an individual other than the analyst to perform the function of QC sample preparation and QC data reduction.

6. When sample breakthrough constitutes more than 25% of the sample mass on the backup section of the sorbent tube, the sample should be invalidated.

7. The order of the analysis of standards and samples should be randomized to remove detector drift as a source of bias in the analysis. Currently, standards are analyzed only before and after samples are analyzed. In this situation, detector drift during the analysis is not compensated for.

B. Industrial Hygiene Recommendations:

1. Observation of the location of exhaust ventilation takeoffs in the vaults along with reports of strong irritant vapors accumulating during the evening and night shifts when there is no activity in the vaults suggests that the current exhaust configuration is of limited effectiveness. An initial recommendation is to lower the exhaust takeoffs to a level closer to the floor, such as 12 to 18 inches, allowing removal of the accumulated contaminant vapors during still periods in the vaults. This would assist with removal of vapors from the dead air spaces between the stacks of notes.

2. Although a large number of the personal exposure samples were not definitive concerning individual formaldehyde exposures, the presence of this compound was confirmed and quantitated in area samples at levels at or above those associated with irritant symptoms. Sampling to evaluate formaldehyde levels should use a method sensitive down to 0.06 mg/m$^3$ (0.05ppm). This generally requires the use of impinger sampling with a 1% sodium bisulfite solution, e.g. NIOSH Method 3500(1) when evaluating future formaldehyde levels in the mechanical examining area. The objective of such sampling is to determine whether formaldehyde levels are below those associated with irritant symptoms. In the event that formaldehyde exposures exceed OSHA's action level of 0.6 mg/M$^3$ (0.5 ppm), all pertinent aspects of OSHA Standard 29 CFR 1910.1048 shall be adhered to.

3. Discussions with the Technical Services Division concerning introducing local exhaust systems and increasing air flows through the examining areas indicated that the requirements to regulate temperature and humidity within fairly narrow ranges and security constraints prevent consideration of readily available options for removing low levels of aldehydes. A heavy dependence upon recirculation of air in this area is standard procedure. In view of these considerations, the approach to removing potential irritants from the work areas will need to include reducing or eliminating the presence of formaldehyde offgassing from the currency paper. This recommendation is one only the bureau itself will be capable of exploring with assistance from their paper manufacturer and supplier. Longer holding of printed currency to permit offgassing of contaminants is probably of limited utility since the currency must be secured by tightly locking down the sheets in a load during periods of storage reducing the total surface area that could release formaldehyde and the other aldehydes.

## IX. REFERENCES

1. National Institute for Occupational Safety and Health. NIOSH manual of analytical methods. 3rd ed. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1984. (DHHS (NIOSH) publication no. 84-100).

2. National Institute for Occupational Safety and Health. NIOSH/OSHA pocket guide to chemical hazards. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1981. (DHHS (NIOSH) publication no. 78-210).

3. American Conference of Governmental Industrial Hygienists. Threshold limit values and biological exposure indices for 1987-1988. Cincinnati, Ohio: ACGIH, 1987.

4. Occupational Safety and Health Administration. OSHA safety and health standards. 29 CFR 1910.1000. Occupational Safety and Health Administration, revised 1983.

5. National Research Council. Formaldehyde and other aldehydes. Washington, D.C.: Committee on Aldehydes, National Research Council, 1981. (National Academy Press).

6. Proctor NH, Hughes JP. Chemical hazards of the workplace. Philadelphia: J.B. Lippencott Company, 1978.

7. American Conference of Governmental Industrial Hygienists. Documentation of the threshold limit values and biological exposure indices. 5th ed. Cincinnati, Ohio: ACGIH, 1986.

8. International Labour Office. Encyclopaedia of occupational health and safety. Vol I/a-k. Geneva: International Labour Office, 1983.

9. National Institute for Occupational Safety and Health. Criteria for a recommended standard: occupational exposure to formaldehyde. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1977. (DHEW publication no. (NIOSH) 77-126).

10. National Institute for Occupational Safety and Health. Testimony of the National Institute for Occupational Safety and Health on the Occupational Safety and Health Administration proposed rule: occupational exposure to formaldehyde 29 CFR 1910 docket no. H-225A. Atlanta, Georgia: National Institute for Occupational Safety and Health, 1986.

11. National Institute for Occupational Safety and Health. Current intelligence bulletin 34–Formaldehyde: Evidence of carcinogenicity. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1981. (DHHS (NIOSH) publication no. 81-111).

12. Department of Labor, Occupational Exposure to Formaldehyde, Final Rule, Federal Register, Volume 52, No. 233, December 4, 1987, pgs. 46168-46312.

13. Sax NI, Lewis RJ, eds. Hawley's condensed chemical dictionary. New York: Van Nostrand Reinhold Co., 1987.

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2. NIOSH Boston Region
3. OSHA, Region III

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# Table I

## Qualitative Analytical Results for Bureau Submitted Test Chamber Samples

U.S. Department of the Treasury
Bureau of Engraving and Printing
Washington, D.C.
HETA 87-266

August 19-20, 1987

| Bureau Sample No.(1) | Total Hydrocarbons(2) in mg/sample |
|---|---|
| C337-Empty Sampling Chamber | 2 |
| C339 | 9 |
| C343 | 7 |
| C354-Regular Production | 8 |
| C359 | 4 |
| C363 | 6 |
| C376 | 5 |
| C380 | 6 |
| C392 | 2 |
| C393 | 4 |
| C413-Test Ink 8/19/1987 | 6 |
| C433-Test Ink 8/20/1987 | 5 |

1. Sample numbers are those used by the bureau. Samples that correspond to inks used on currency evaluated during the NIOSH survey are noted to the right of the sample number and the date exposure monitoring was conducted, not the date of the bureau°s collection of the test sample listed here.

2. Values are estimates of the total hydrocarbons present using the sum of all peak areas including aldehydes for calculations. A mineral spirits bulk was used as a standard for comparison.

## Table II

### Personal Exposure and Area Sampling Results for Formaldehyde, Butanal, Pentanal, and Hexanal

Bureau of Engraving and Printing
Washington, D.C.

HETA 87-266
August 1987

| Sample Description(1) | | | Contaminant Concentration in mg/m$^3$(2) | | | | | |
|---|---|---|---|---|---|---|---|---|
| Date | Machine | Location or Job | Type | Volume | Formaldehyde | Butanal | Pentanal | Hexanal |
| Regular Currency Production: | | | | | | | | |
| 8/19 | 972 | A3 Face examining station | A | 20 | Trace | 1.1 | Trace | Trace |
| | | A3 Face examiner | P | 20 | N.D. | 0.98 | Trace | Trace |
| | | A1 Face examiner | P | 19 | N.D. | 1.2 | Trace | Trace |
| | | A3 Back exminer | P | 18 | Trace | 1.4 | Trace | Trace |
| | | A1 Back examiner | P | 19 | Trace | 1.3 | Trace | Trace |
| | | Book binder | P | 20 | N.D. | 1.3 | Trace | Trace |
| 8/20 | 972 | A3 Face examining station | A | 19 | N.D. | Trace | Trace | Trace |
| | | A3 Face examiner | P | 21 | Trace | 1.1 | Trace | Trace |
| | | A1 Face examiner | P | 21 | N.D. | 0.92 | Trace | Trace |
| | | A3 Back examiner | P | 12 | N.D. | Trace | Trace | Trace |
| | | A1 Back examiner | P | 21 | N.D. | 0.95 | Trace | Trace |
| | | Book binder | P | 22 | N.D. | 1.1 | Trace | Trace |
| 8/19 | 978 | A3 Face examining station | A | 23 | N.D. | Trace | Trace | Trace |
| | | A1 Face examiner(3) | P | 20 | N.D. | Trace | Trace | Trace |
| | | A3 Back examiner | P | 19 | N.D. | Trace | Trace | Trace |
| | | A1 Back examiner | P | 19 | N.D. | Trace | Trace | Trace |
| | | Book binder | P | 21 | N.D. | 0.85 | Trace | Trace |
| | | Stacker | P | 21 | N.D. | Trace | Trace | Trace |
| 8/20 | 978 | A3 Face examining station | A | 25 | N.D. | Trace | Trace | Trace |
| | | A3 Face examiner | P | 21 | N.D. | Trace | Trace | N.D. |
| | | A1 Face examiner | P | 21 | N.D. | Trace | Trace | N.D. |
| | | A3 Back examiner | P | 23 | N.D. | Trace | Trace | N.D. |
| | | A1 Back examiner | P | 21 | N.D. | Trace | Trace | Trace |
| | | Book binder | P | 23 | N.D. | Trace | Trace | Trace |
| Test Currency Production: | | | | | | | | |
| 8/19 | 976 | Air knife-initial currency feed | E | 17 | N.D. | Trace | Trace | Trace |
| | | A3 Face examining station | A | 20 | N.D. | Trace | Trace | Trace |
| | | Above A3 Back feed line | A | 19 | N.D. | Trace | Trace | Trace |
| | | A3 Face examiner | P | 15 | N.D. | Trace | Trace | N.D. |
| | | A1 Face examiner(4) | P | 14 | N.D. | Trace | Trace | N.D. |
| | | Book binder | P | 15 | N.D. | Trace | N.D. | N.D. |

(continued)

## Table II (continued)

## Personal Exposure and Area Sampling Results for Formaldehyde, Butanal, Pentanal, and Hexanal

Bureau of Engraving and Printing
Washington, D.C.

HETA 87-266
August 1987

| Sample Description(1) | | | Contaminant Concentration in $mg/m^3$(2) | | | | | |
|---|---|---|---|---|---|---|---|---|
| Date | Machine | Location or Job | Type | Volume | Formaldehyde | Butanal | Pentanal | Hexanal |
| Regular Currency Production: | | | | | | | | |
| 8/20 | 976 | Air knife-initial currency feed | E | 25 | N.D. | Trace | Trace | N.D. |
| | | A3 Face examining station | A | 23 | N.D. | Trace | Trace | N.D. |
| | | Above A3 Back feed line | A | 23 | N.D. | Trace | Trace | Trace |
| | | A3 Face examiner | P | 15 | N.D. | Trace | N.D. | N.D. |
| | | A1 Face examiner(4) | P | 15 | N.D. | Trace | N.D. | N.D. |
| | | Book binder | P | 15 | N.D. | N.D. | N.D. | N.D. |
| Calculated Environmental Limit of Detection:(5) | | | | | 0.67 | 0.33 | 0.34 | 0.50 |
| Calculated Environmental Limit of Quantitation:(6) | | | | | 2.1 | 1.4 | 1.4 | 1.8 |
| Evaluation Criteria: NIOSH(7) | | | | | L.F.L.[8] | --- | --- | --- |
| ACGIH | | | | | 1.5[9] | --- | 175[11] | --- |
| OSHA | | | | | 1.2[10] | --- | --- | --- |

1. Sample Description: Date sampling conducted. Machine number denotes the mechanical examining station, each with four examining stations, a book binder and a stacker. Sample location or job designates were sample obtained on that machine. Type denotes whether the sample is an Area sample, Personal exposure sample, or a procEss sample. Volume denotes the total volume of air sampled over the work shift in liters, using a sampling flow rate of 50 cubic centimeters per minute.
2. Contaminant Concentration: Given in milligrams per cubic meter of air sampled ($mg/m^3$). Trace indicates that the contaminant was present above the analytical limit of detection, but below a level that could be accurately quantified. N.D. denotes that the contaminant, if present, was below the analytical limits of detection.
3. The A3 Face examiner on this machine was not sampled 8/19/1987 because worker was smoking at the work station.
4. For the test currency only the currency face had been printed, therefore there were only face examiners present these machines while the currency examined.
5. The calculated environmental limit of detection is the highest level that the contaminant may have been present in any of the samples without being identified as present. Note that the larger the sample volume the lower the limit of detection, therefore some samples may indicate trace quantities or numerical values below the ones presented on this line. This value is obtained using the smallest sample volume for which a N.D. value was determined.
6. The calculated environmental limit of quantitation denotes the highest quantity of contaminant that can be present among the samples designated as having trace concentrations. This is again influenced by sample size as mentioned previously. It is determined by dividing the analytical limit of quantitation for each respective analyte by the smallest sample volume exhibiting detectable but nonquantifiable concentrations of the analytes.
7. Sources for evaluation criteria: NIOSH-National Institute for Occupational Safety and Health reference 2; ACGIH-American Conference of Governmental Industrial Hygienist°s Threshold Limit Values$^{é}$ reference 3; and OSHA-Occupational Safety and Health Administration Permissible Exposure Levels, reference 4.
8. L.F.L.: Denotes that formaldehyde is considered a potential occupational carcinogen and exposures should be maintained at the lowest feasible level, reference 10,11.
9. ACGIH lists formaldehyde as a suspected human carcinogen to which exposures should be kept to a minimum, reference 3.
10. OSHA considers formaldehyde a probable human carcinogen. All provisions of the revised standard (29 CFR 1910.1048 shall be followed if exposures exceed the action level of 0.6 $mg/M^3$ (0.5 ppm). (See reference 12).
11. Pentanal is listed in the ACGIH reference as n-valeraldehyde.

# Table III
# Area Sample Results for Solvents and Formaldehyde at Currency Examination Machines
Bureau of Engraving and Printing
Washington, D.C.

HETA 87-266
August 1987

| Sample Description(1) | | | | Contaminant Concentration in mg/m$^3$(2) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Date | Machine | Location | Duration | $CH_3COCH_3$ | $CCl_3CH_3$ | Toluene | Min Spirits | Kerosene | HCHO |
| Regular Currency Production: | | | | | | | | | |
| 8/19 | 972 | A3 Face examining station | 386 | Trace | N.D. | N.D. | 63 | 12 | 0.25 |
| 8/20 | 972 | A3 Face examining station | 431 | N.D. | N.D. | N.D. | 27 | 5.2 | 0.20 |
| 8/19 | 978 | A3 Back examining station | 371 | Trace | N.D. | Trace | 32 | 5.6 | 0.17 |
| 8/20 | 978 | A3 Face examining station | 444 | Trace | N.D. | Trace | 26 | 4.2 | 0.13 |
| Test Currency Production:(3) | | | | | | | | | |
| 8/19 | 976 | A3 Face examining station | 327 | --- | --- | --- | --- | --- | 0.17 |
| | | Above A3 Back feed line | 326 | Trace | N.D. | Trace | 18 | Trace | 0.18 |
| 8/20 | 976 | A3 Face examining station | 442 | --- | --- | --- | --- | --- | 0.18 |
| | | Above A3 Back feed line | 447 | N.D. | N.D. | Trace | 24 | 4.4 | 0.16 |
| Evaluation Criteria:(4) | NIOSH | | | 590 | 1900 | 375 | 350 | 100 | LFL* |
| | ACGIH | | | 1780 | 1900 | 375 | --- | --- | 1.5** |
| | OSHA | | | 2400 | 1900 | 750 | --- | --- | 1.2*** |

1. Sample Description: Date sampling conducted. Machine number denotes the mechanical examining station, each with four examining stations, a book binder and a stacker. Sample location designates were the sample was obtained on that machine.
2. Contaminant Concentration: Given in milligrams per cubic meter of air sampled (mg/m$^3$). Trace indicates that the contaminant was present above the analytical limit of detection, but below a level that could be accurately quantified. N.D. denotes that the contaminant, if present, was below the analytical limits of detection.
3. For the test currency only the currency face had been printed.
4. Sources for evaluation criteria: NIOSH-National Institute for Occupational Safety and Health reference 2; ACGIH-American Conference of Govemmental Industrial Hygienist°s Threshold Limit Values$^{é}$ reference 3; and OSHA-Occupational Safety and Health Administration Permissible Exposure Levels, reference 4.

* L.F.L.: Denotes that formaldehyde is considered a potential occupational carcinogen and exposures should be maintained at the lowest feasible level, reference 10,11.

** ACGIH lists formaldehyde as a suspected human carcinogen to which exposures should be kept to a minimum, reference 3.

*** OSHA considers formaldehyde a probable human carcinogen. All provisions of the revised standard (29 CFR 1910.1048) be followed if exposures exceed to action level of 0.6 mg/M$^3$ (0.5 ppm). (see Reference 12).

SeQ6002
C413/$CS_2$

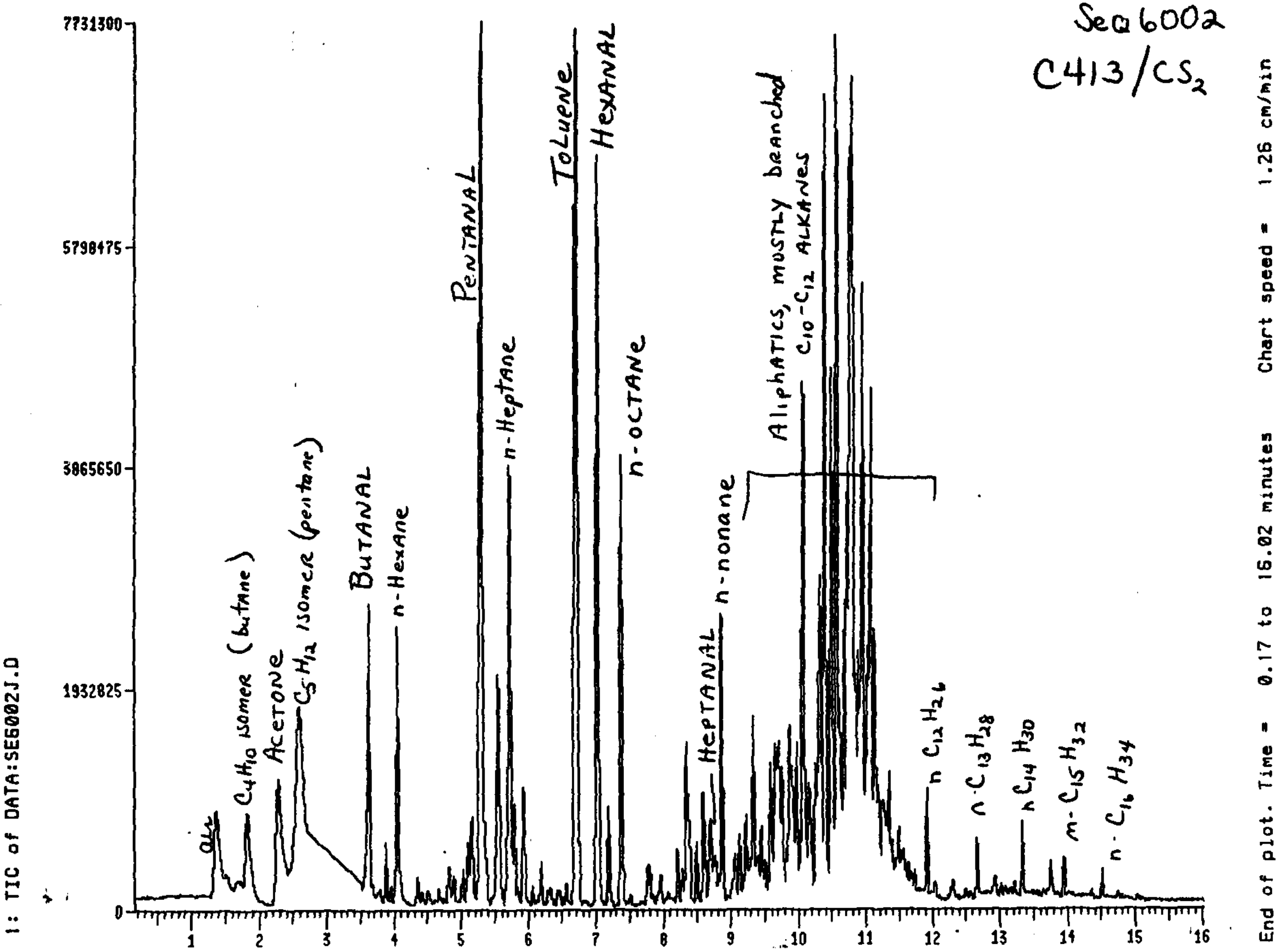


FIGURE 1
Test Sample - Ink Formula #AL217627
Collected by BEP, August 10, 1987

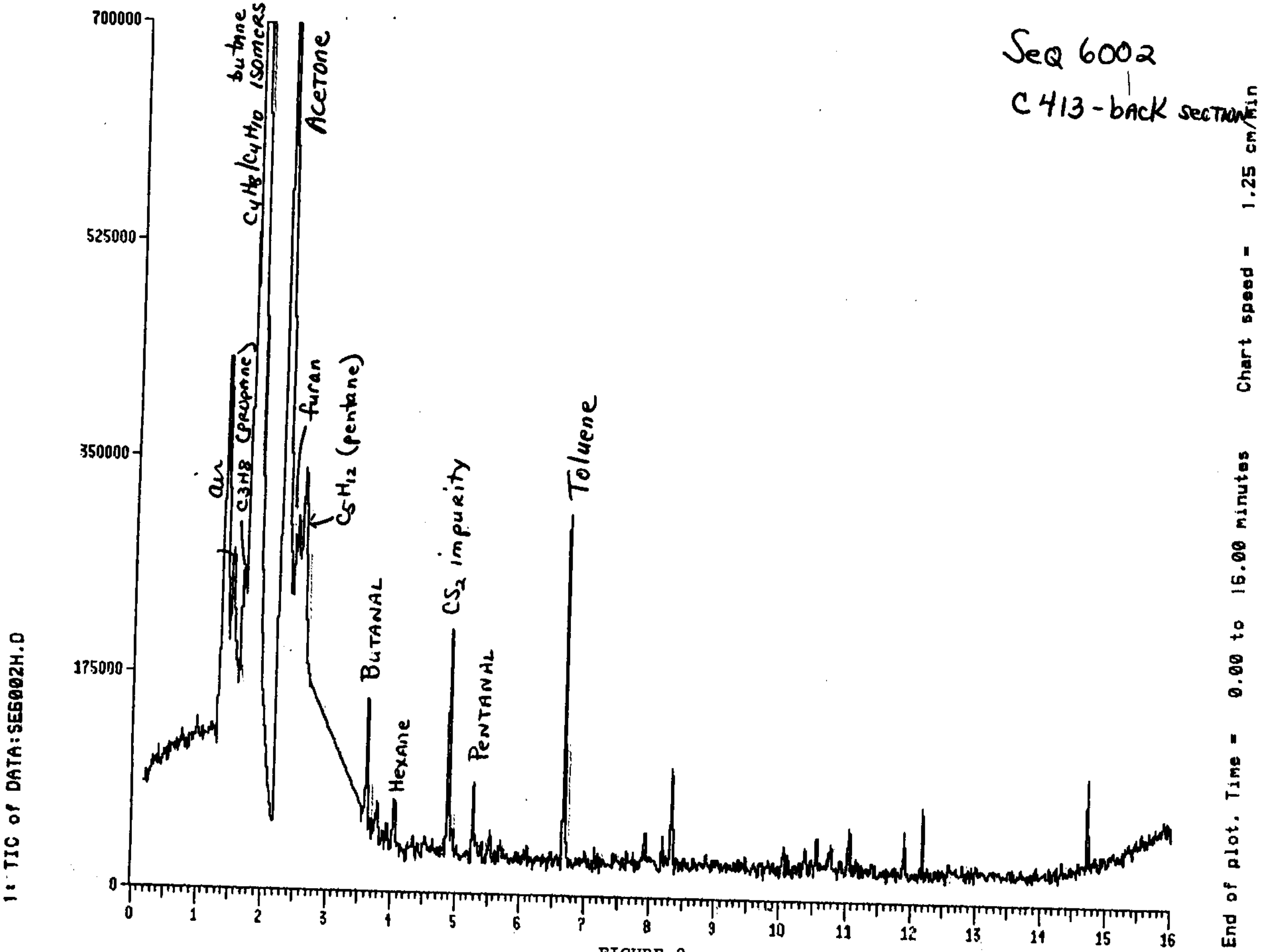


FIGURE 2
Back-up Section of Sample C-413,
Ink Formula No. AL217627

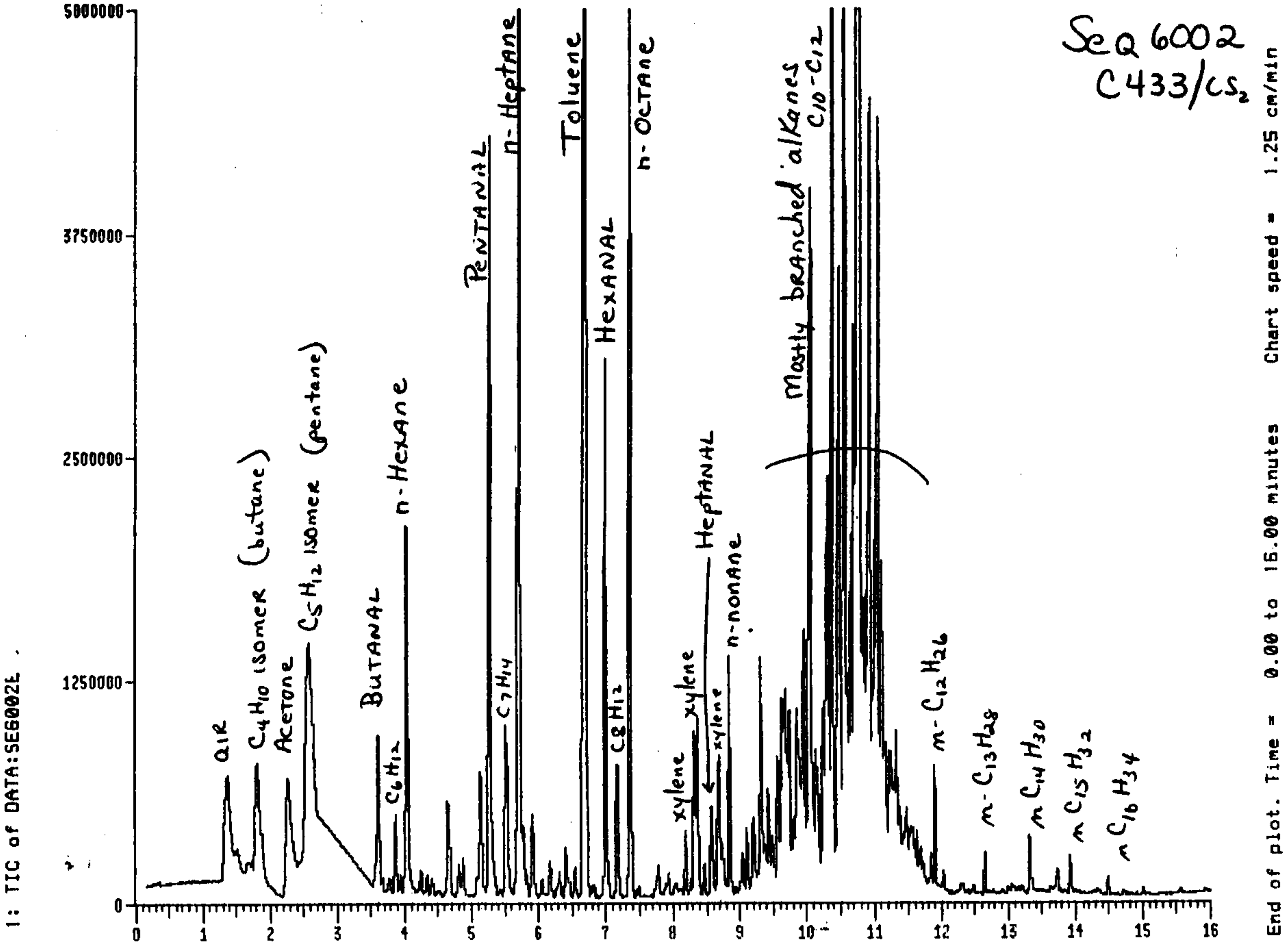


FIGURE 3
Test Sample Collected August 11, 1987,
Ink Formula No. AL215608

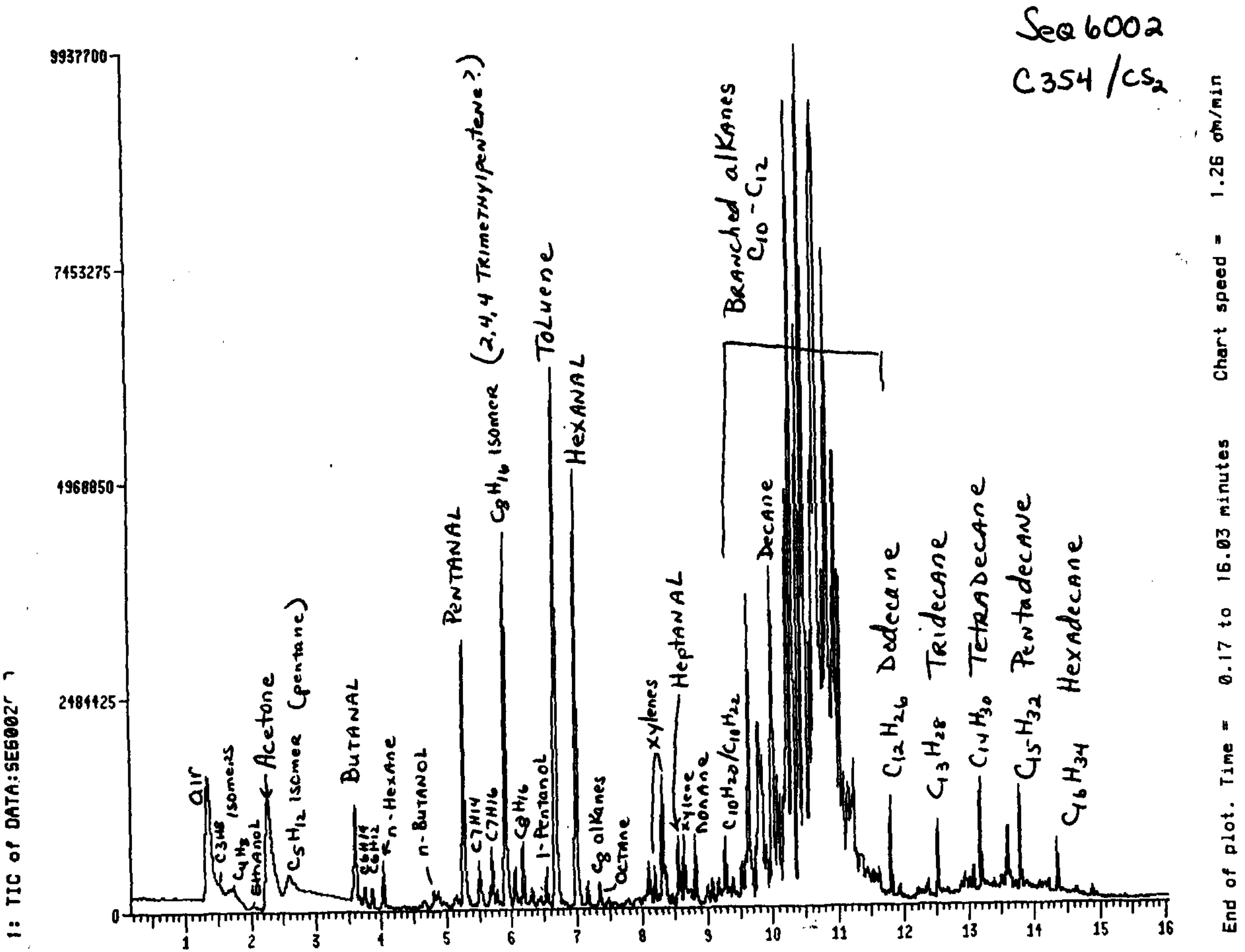


FIGURE 4
BEP Test Sample Collected
August 7, 1987-Regular Production Ink

Seq 6002
C354- back section

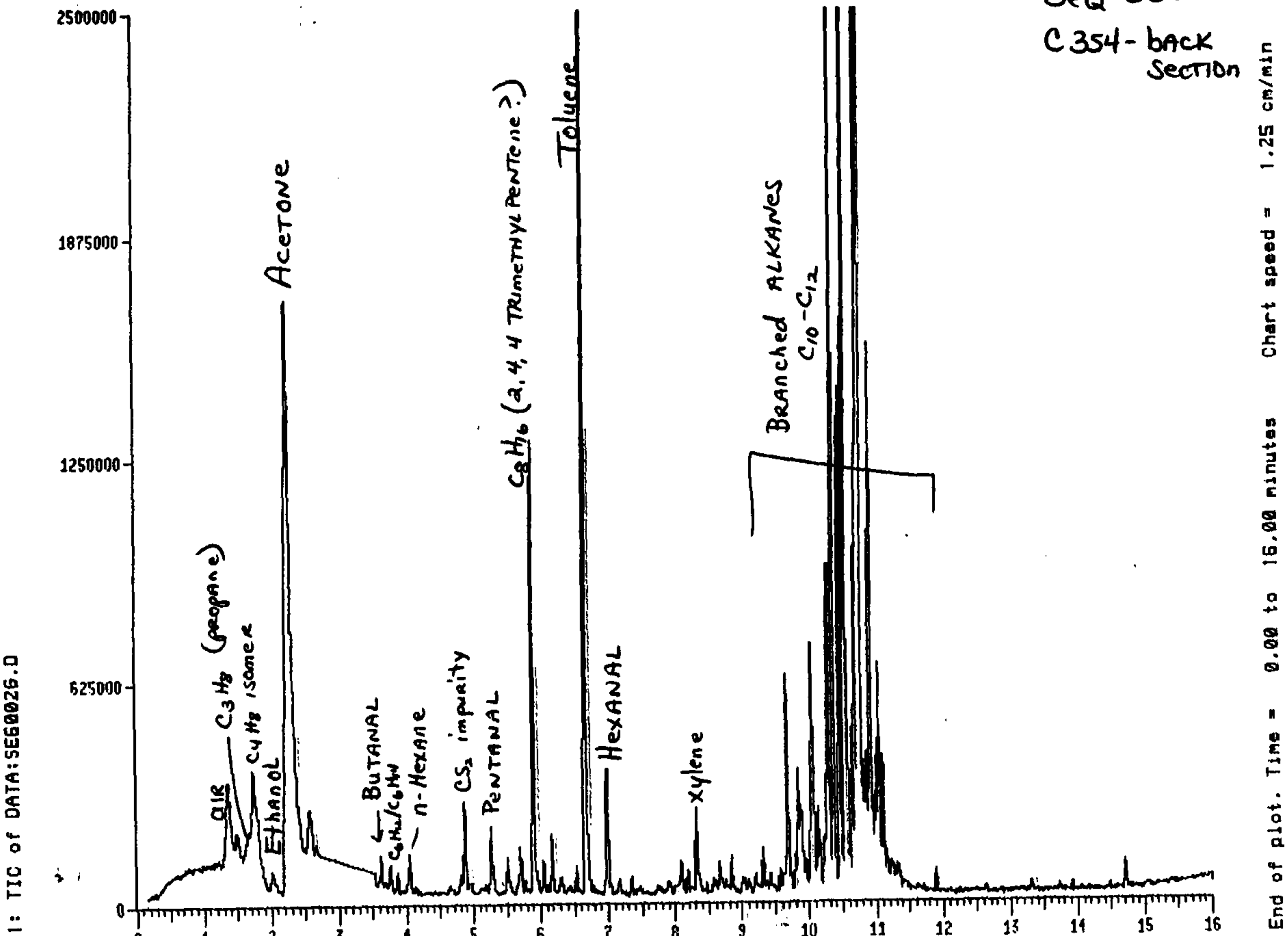
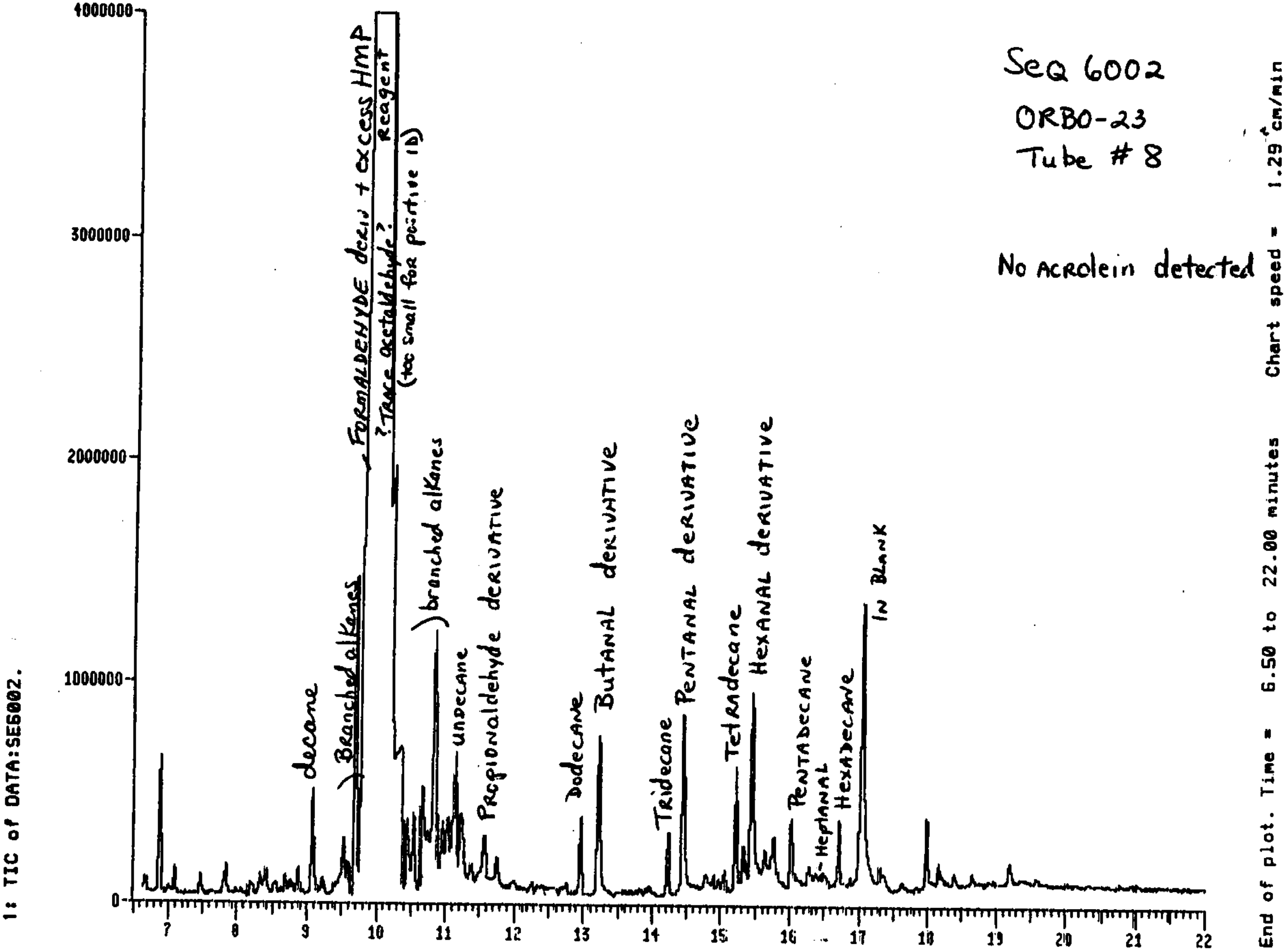


FIGURE 5
Back-up Section for Regular Production Ink Sample
Collected August 7, 1987, by BEP



Seq 6002
ORBO-23
Tube # 8

No acrolein detected

FIGURE 6
Representative for Aldehyde Confirmation, Area Samples at the
A3 Face Examining Station, August 19-20, 1987

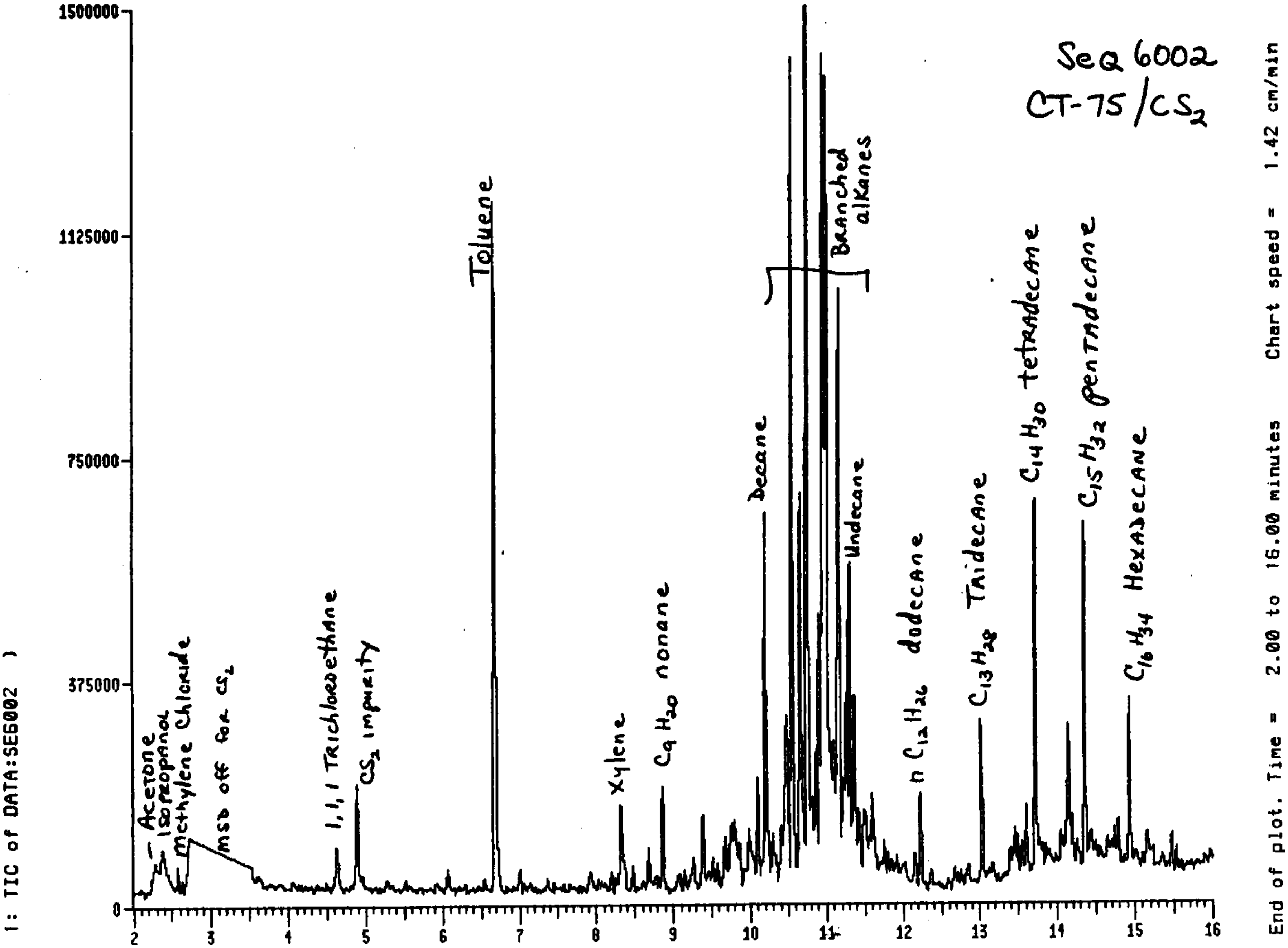


FIGURE 7
Representive Solvent Vapor Composition of Area Samples
August 19-20, 1987, in Mechanical Examining

# Appendix A
## Bureau of Engraving and Printing Draft Method for Aldehydes

PREFACE:

This method was originated from two NIOSH Analytical methods: #2501 (for acrolein) and #2502 (for formaldehyde). Method 2502 has been modified to include the analysis of homologs of formaldehyde, so that acetaldehyde, butanal, pentanal, hexanal, and heptanal can be determined as well.

No research effort was performed to evaluate the method applicability, detection sensitivity, trapping efficiency, and desorption efficiency, etc.

A chemist must become fimiliar with both NIOSH analytical methods before making effort to analyze the homologous series of formaldehyde.

SAMPLING:

SAMPLER: SOLID SORBENT TUBES:

1. For acrolein: 2-(hydroxymethyl) piperidine on XAD-2, 120mg/60mg.
2. For saturated aldehydes: 2-(benzylamino) ethanol on XAD-2, 120mg/60mg.

FLOW RATE: 50 mL/min.
VOLUME: 15 or 18 liters
SAMPLE STABILITY: 4 weeks @ 25°c.
BLANKS: Plain Paper, Empty Bag, and ambient air.

INSTRUMENTATION:

A. FOR SATURATED LOW MOLECULAR WEIGHT ALDEHYDES:
TECHNIQUE: Capillary gas chromatography, NPD
ANALYTE: 3-benzyloxazolidine derivatives
DESORPTION: 1.70 mL toluene; ultrasonic bath for 10 minutes
INJECTION VOLUME: 0.5 uL for front section, 1.0 uL for rear section; splitless for 30 seconds.

TEMPERATURE:

INJECTOR: 230°C
DETECTOR: 275°C

COLUMN: 70°C for 30 seconds; 8°C/min, hold at 220°C for 3 minutes, then 10°C/min, hold at 250°C for 1 minute.

EQUILIBRATION: 4 minutes

CARRIER GAS: Helium, 85 kPa, make-up flow, 5ml/min.

COLUMN: Fused silica capillary, 30 m x 0.25 mm id. SP-2250 (equivalent to OV-17, 50:50 methyl:phenyl silicone.

CALIBRATION: Mixture of 3 benzyloxazolidine derivatives in toluene.

RANGE: 5.8 to 625 ug per sample.

B. FOR ACROLEIN:

## REAGENTS:

1. Eluent: toluene, Fisher certified ACS
2. Formalin solution: 37%
3. Acetaldehyde
4. Butanal
5. Pentanal
6. Hexanal
7. Heptanal
8. Acrolein

## EQUIPMENT:

1. Sampler: for saturated low molecular aldehydes: 10cm x 4mm id glass tubes containing a 120-mg fron section and a 60-mg back-up section of 2-(benzylamino) ethanol on XAD-2 beads (ORBO-22) for acrolein, 2-(hydroxymethlyl) piperidine on XAD-2 beads (ORBO-23). Both were supplied by Supelco Inc.
2. Gilian personal sampling pump, connected with dual sampling ports, for simultaneously sampling saturated and unsaturated aldehydes. All pumps were calibrated at 50 mL/min.
3. Gas Chromatographs with packed column and capillary column injectors, NPD, and automatic sample injector. Hewlett Packard Model 5890 was used in this laboratory.
4. reaction vials, 4-ml with miminert valves
5. sample vials
6. crimp seals, crimper, and decaper
7. bubble meter for flow rate calibration
8. Syringe: 10 uL, readable to 0.1 uL
9. Repipet Dispenser, 5-ml from LAB INDUSTRIES
10. Ultrasonic vibrator

## SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the smapler immediately before sampling. Attached sampler to personal sampling pump with flexible tubing.
3. Sample at 0.05 L/min for 6 hours for a total sample size of 18 L, (Total sample volume depend on concentration of aldehyde in the air).
4. Cap the samplers with plastic (not rubber) caps and pack securely until laboratory analysis.

## SAMPLE PREPARATION:

1. Score each sampler with a file in front of the front sorbent section.
2. Break sampler at score line. discard glass wool plug and transfer the front sorbent in a vial.
3. Transfer the rear section to another vial.
4. Add 1.7 mL eluent to each vial. Screw cap tightly onto each vial.
5. Agitate vials in an ultrasonic bath for at least 10 minutes.

## CALIBRATION AND QUALITY CONTROL:

A. CALIBRATION WITH WORKING STANDARDS

1. For acrolein:
   a. Break the sampler only at the front section.
   b. Inject a known volume of acrolein solution onto the glass wook, cap the sampler and allow to sit overnight at room temperature.
   c. Open a rear end and attach the sampler to personal air sampling pump, remove the cap in front of the sampler, allow air flow through the sampler for 2 to 3 seconds.
   d. Remove the sampler and cap both sides with plastic caps.
   e. Follow the procedures in sample preparation before GC analysis.

2. For saturated aldehydes:
   a. Transfer all the XAD-2 beads from 2 unused samplers into a 4-mL reaction vial, add 4 mL toluene into the vial and cap it with mininert valve.
   b. Use 10 uL syringe to add known amount of each aldehyde into toluene solution. After all the aldehyde of interest is added, shake the solution well, and place in ultrasonic bath for 10 minutes . Allow the solution to site overnight. Be cautious to avoid the air space developed in the syringe when the more viscous aldehyde, are sampled. For acetaldehyde, both the syring and the aldehyde have to be refrigerated for at least 10 minutes before sampling.
   c. The following day, dilute the stack solution in order to prepare 3 standard solutions bracketing the sample concentration range diluted from the 4mL toluene solution for GC analysis.
   d. Analyze the 3 standard solutions before and after a batch of samples (the number of samples in a batch depends on the stability of the NPD detector).
   e. Prepare calibration graph and regression analysis based on the peak area and the concentration (ug/mL) of the aldehyde of interest. The origin can be included in the regression analysis except for formaldehyde which has inherent background in the sampler.

## GC ANALYSIS:

A. Set gas chromatograph to conditions listed in Instrumentation section of this report. Set air and hydrogen flow rates on the Nitrogen specific detector to manufacturer's specifications. Inject 0.5-uL sample aliquot.

B. Identify each peak in the chromatogram.

C. Measure the peak areas of interest.

## CALCULATIONS:

A. From the calibration curve, determine the quantity (in ug/mL) of each aldehyde found in the sample front ($W_f$) and back ($W_b$) sorbent sections and multiply by the desorption volume, (1.7 mL).

B. Calculate the concentration, Cm (mg/m$^3$), of each aldehyde in the air sample, using the following formula:

$$C_m = \frac{(W_f + W_b) \times 1.7}{V}, \text{ (mg/m}^3\text{: milligram per cubic meter)}$$

Because the working standards are prepared on media blanks, no additional blank correction is necessary.

3. The concentration may also be expressed in terms of parts per million by volume (C):

$$\frac{C_m \times 24.45}{MW}, \text{ in ppm}$$

Where: Cm=air concentration found from previous step.
24.45=molar volume at standard conditions.
MW=Molecular weight of the aldehyde of interest.
V=Volume of air sampled.