LOW COST DETECTOR OF FORMALDEHYDE AND IONIZABLE VOCS (TVOC) FOR THE HOMEOWNER AND HOME INSPECTOR

HTIP REPORT
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ABSTRACT

The literature was reviewed, and summarized, in an effort to find new and novel approaches for the measurement of formaldehyde at levels typically found indoors. This information was organized in the form of an annotated bibliography, and a technical summary, and is presented in the appendix of this report.

The review focused, in particular, on identifying simple low cost methods for ionizing molecules and two methods, one based on a heated platinum catalyst, and a second, based on vacuum ultraviolet light, were selected for further study. Both sources produce ions only in the presence of organic materials and, when combined with a low cost ion detector such as an electroscope, provide the basis for sensitive low cost detectors for formaldehyde and VOCs.

This research project covered the development and testing of several portable detectors based on the platinum catalyst and vacuum ultraviolet (VUV) source-electroscope combinations. The research effectively demonstrated that both technologies can detect volatile organic carbon materials and formaldehyde at very low concentrations. The performance of both prototypes was better than expected and, it was possible to measure formaldehyde at or below 0.05 parts per million, the Health and Welfare Canada long term exposure guideline. Several modifications were proposed which should increase sensitivity and lower the minimum level detectable even further, but more care must be taken to minimize chemical background and, to better control the experimental conditions.

The prototypes were not selective, and responded to acetone, a typical volatile organic carbon, as well as to formaldehyde. Although some additional work is required to make the detectors more selective, this research has proven the feasibility of developing simple, sensitive, low cost detectors for volatile organic carbon materials. There is a need at the present time for low cost survey type detectors of this nature.

EXECUTIVE SUMMARY

The literature was reviewed, and summarized, in an effort to find new and novel approaches to the measurement of formaldehyde at levels typically found indoors. This information was organized in the form of an annotated bibliography, and technical summary, and is presented in the appendix of this report.

Methods of ionizing organic molecules, in particular, those methods which could be used with a charge measuring device such as an electroscope, were evaluated on the basis of several criteria. They should: generate an ion current in proportion to the level of VOC present; be safe; be relatively inexpensive; be reliable; be stable; be effective; and only generate currents in the presence of a VOC.

Two promising ion sources, one based on a heated platinum catalyst, and a second based on a vacuum ultraviolet light source (VUV), were selected for further study. Both sources produce ions only in the presence of organic materials, and, when combined with a low cost ion measuring device such as an electroscope, provide the basis for sensitive low cost detectors for formaldehyde and VOCs.

Small leaf type electroscopes, comprised of an aluminum foil leaf, a stainless steel center electrode mounted in a teflon insulator, a means for injecting samples of formaldehyde and volatile organic carbon materials into the electroscope, a means for applying a charge to the center electrode, and a means for reading out the angle of deflection of the leaf or the state of charge, were developed as means for detecting and measuring ions produced by the sources.

Several prototype detectors were constructed, based on the platinum catalyst and VUV ion sources, combined with leaf electroscopes. The platinum catalyst ion sources were constructed from small pieces of platinum wire, heated to about 800 C degrees, and mounted inside the electroscope, about 3 cm from the leaf electrode. The VUV sources were based on a corona discharge in a flowing argon gas stream. The VUV source was located external to the electroscope and the VUV light produced by the source passed through a window into the electroscope.

The samples to be measured were introduced into the electroscope by various means and at different concentrations. Inside the electroscope, the samples were ionized by either the heated platinum catalyst or the VUV sources and, the ions so produced were attracted to the electrically charged leaf electrode. Some of the charge on the leaf electrode was, as a result, neutralized. The angle of deflection of the leaf changed in proportion to the amount of ionic charge collected, the ionic charge being related to the concentration of the sample present in the electroscope.

The performance of the platinum catalyst prototype detector was better than expected and, it was possible to measure formaldehyde at or below 0.01 parts per million, the Health and Welfare Canada long term exposure guideline, and over the range of concentrations from 0.01 to 2.5 parts per million. With improvements, formaldehyde concentrations below 0.01 parts per million should be easily measured but, more care must be taken to minimize chemical background and to better control experimental conditions.

The VUV prototypes detected formaldehyde down to 0.03 parts per million and the response increased with increasing concentration in the range from 0.03 to 0.533 parts per million. Results were less reproducible than for the platinum catalyst detector and, the response tended to saturate above 1 part per million. An increased range of performance is expected by increasing the ultraviolet light output of the source and by exposing more of the sample to ultraviolet light. Both changes should increase the production of ions and prevent saturation at higher formaldehyde concentrations.

None of the prototypes were able to discriminate between acetone, which is a typical volatile organic carbon (VOC), and formaldehyde, and additional work is required to achieve better specificity. Results at the present time, however, demonstrate the feasibility of developing very sensitive low cost VOC detectors by combining a platinum catalyst or VUV based ion source with an ion detector such as an electroscope. Although the proposed VOC detectors are not selective in response, there are many applications in indoor air quality investigations where non specific low cost survey type VOC detectors are needed. At the present time, there are no survey type detectors with enough sensitivity to measure VOCs at levels typically found in residences.

RÉSUMÉ

La documentation a été examinée et résumée dans le but de trouver des façons innovatrices de mesurer les concentrations de formaldéhyde que l'on retrouve généralement à l'intérieur. L'information a été présentée sous forme de bibliographie commentée et de résumé technique annexés au présent rapport.

L'examen consistait en particulier à trouver des méthodes peu coûteuses d'ionisation des molécules et deux méthodes, une fondée sur le catalyseur au platine chauffé et l'autre sur l'ultraviolet extrême, ont fait l'objet d'études plus approfondies. Les deux sources produisent des ions seulement en présence de composés organiques et lorsqu'elles sont combinées à un détecteur d'ion peu coûteux comme un électroscope, elles fournissent le nécessaire pour détecter le formaldéhyde et les composés organiques volatils (COV).

Ce projet de recherche portait sur la conception et la mise à l'essai de plusieurs détecteurs portatifs fondés sur le catalyseur au platine et les combinaisons entre l'ultraviolet extrême et l'électroscope. La recherche a démontré de façon efficace que les deux méthodes réussissent à détecter des produits contenant du carbone organique volatil et du formaldéhyde à des concentrations très faibles. La performance des deux prototypes a été meilleure que celle à laquelle on s'attendait et il était possible de mesurer des taux de formaldéhyde en deçà de 0,05 ppm, la directive d'exposition à long terme de Santé et Bien-être social Canada. Plusieurs modifications proposées permettraient d'augmenter la sensibilité et de diminuer considérablement le taux minimum détectable. Toutefois, un plus grand soin doit être apporté afin de minimiser l'accumulation de produits chimiques et avoir la main mise sur les conditions d'expérimentation.

Les prototypes n'étaient pas sélectifs et ont réagi à l'acétone, un carbone organique volatil typique ainsi qu'au formaldéhyde. Même si des travaux supplémentaires sont requis pour améliorer la sélectivité des détecteurs, cette recherche a prouvé qu'il était possible de créer des détecteurs simples, sensibles et peu coûteux à l'égard des composés organiques volatils. En ce moment, le besoin d'un tel type de détecteur peu coûteux se fait sentir.

RÉSUMÉ

Nous avons passé en revue la documentation et l'avons résumée dans le but de trouver des façons nouvelles et innovantes de mesurer le formaldéhyde à des concentrations que l'on trouve normalement en milieu intérieur. Nous avons ensuite organisé cette information sous la forme d'une bibliographie annotée et d'un résumé technique que nous présentons en annexe du présent rapport.

Nous avons évalué, selon plusieurs critères, des méthodes permettant d'ioniser des molécules organiques, en particulier celles qui sont susceptibles d'être employées de concert avec un appareil de mesure de la charge, tel qu'un électroscope. Ces méthodes devaient pouvoir générer un courant ionique proportionnel au composé organique volatil (COV) présent et être sûres, relativement peu coûteuses, fiables, stables et efficaces et ne produire de courant qu'en présence d'un COV.

Nous avons sélectionné deux sources d'ions prometteuses pour poursuivre l'étude : un catalyseur au platine chauffé et une lumière ultraviolette extrême. Les deux sources ne produisent des ions qu'en présence de matières organiques et, lorsqu'elles sont conjuguées avec un électroscope, un appareil économique qui permet de mesurer les ions, elles forment la base de détecteurs économiques et sensibles de formaldéhyde et de COV.

Les petits électroscopes à feuille, comportant une feuille d'aluminium, une électrode centrale en acier inoxydable montée sur un isolant en téflon, un dispositif d'injection des échantillons de formaldéhyde et de COV, un dispositif d'application de la charge à l'électrode centrale ainsi qu'un dispositif de mesure de la déviation angulaire de la feuille ou de l'état de charge, ont été conçus pour détecter et mesurer l'émission d'ions.

Nous avons construit plusieurs prototypes de détecteurs à partir d'électroscopes à feuille faisant appel à un catalyseur au platine ou à une lumière ultraviolette extrême comme source d'ions. Le catalyseur au platine a été réalisé avec des bouts de fils de platine chauffés à une température de près de 800 °C et montés à l'intérieur de l'électroscope à environ 3 cm de la feuille. La lumière ultraviolette extrême a été obtenue grâce à une décharge par effet de couronne au sein d'un flux d'argon. La source lumineuse était située à l'extérieur de l'électroscope et la lumière U.V. passait par une fenêtre de l'électroscope.

Les échantillons à mesurer ont été introduits dans l'électroscope par divers moyens et à différentes concentrations. À l'intérieur de l'appareil, les échantillons étaient ionisés soit par le catalyseur au platine, soit par la lumière ultraviolette extrême, et les ions ainsi produits étaient attirés par la feuille électrisée. Une partie de la charge de la feuille s'en trouvait donc neutralisée. L'angle de déviation de la feuille changeait proportionnellement à la charge ionique accumulée, la charge ionique étant liée à la concentration de l'échantillon introduit dans l'électroscope.

La performance du prototype fonctionnant avec un catalyseur au platine a été meilleure que prévu, et il a été possible de mesurer le formaldéhyde à une concentration de 0,01 mg/L et moins, valeur correspondant à la directive d'exposition à long terme de Santé et Bien-être social Canada,

de même qu'à des concentrations de 0,01 à 2,5 mg/L. Moyennant quelques améliorations, l'appareil devrait facilement pouvoir mesurer des concentrations de formaldéhyde inférieures à 0,01 mg/L, mais il faudra réduire au minimum la présence de substances chimiques ambiantes et mieux maîtriser les conditions d'expérimentation.

Les prototypes basés sur la lumière ultraviolette extrême ont pu détecter des concentrations de 0,03 mg/L, une réponse s'améliorant à mesure que les concentrations augmentaient selon des valeurs d'étendant de 0,03 à 0,533 mg/L. Les résultats se sont avérés moins reproductibles qu'avec le détecteur à catalyseur au platine et la réponse avait tendance à atteindre la saturation à une concentration supérieure à 1 mg/L. Nous croyons pouvoir obtenir une meilleure performance en augmentant l'intensité de la lumière ultraviolette et en exposant une plus grande portion de l'échantillon à la lumière ultraviolette. Ces deux améliorations devraient permettre d'accroître la production d'ions et de prévenir la saturation à des concentrations supérieures de formaldéhyde.

Aucun des prototypes n'a été en mesure de faire la différence entre l'acétone, un COV courant, et le formaldéhyde. Il faudra donc poursuivre les améliorations pour que les appareils soient plus précis. Mais pour l'instant, les résultats obtenus montrent qu'il est possible de mettre au point des détecteurs de COV économiques et très sensibles en alliant un catalyseur au platine ou une lumière ultraviolette extrême, comme source d'ions, avec un détecteur d'ions tel qu'un électroscope. Bien que la réponse des détecteurs de COV proposés ne soit pas sélective, ceux-ci pourraient s'avérer utiles dans bien des études sur la qualité de l'air intérieur qui requièrent l'emploi de détecteurs de COV économiques non spécifiques. À l'heure actuelle, il n'existe aucun détecteur de ce genre suffisamment sensible pour mesurer les COV à des concentrations que l'on trouve habituellement en milieu résidentiel.

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1.0 BACKGROUND STATEMENT

Indoor air quality is becoming an increasing concern as housing becomes tighter, particularly, where ventilation is inadequate. Air pollutants which originate from building materials, furnishings, or occupant activities can affect the health and well being of the occupant.

There is clearly a need to measure and characterize pollutant levels on the part of the home owner or home inspector, particularly in houses or office buildings where air quality is the suspected cause of the problem.

Unfortunately many VOCs and formaldehyde are often at levels which existing instruments and methods cannot measure quickly or accurately. There are simply no instruments commercially available with adequate sensitivity, and speed.

It was the purpose of this investigation to review the literature relating to the measurement of formaldehyde and, to identify methods which offer promise for use in low-cost portable detectors, particularly those which generate ions and may be associated with a simple ion-measuring device such as an electroscope. Vacuum Ultraviolet (VUV) light (11.5 ev) or a heated platinum catalyst source, offer promise in this respect, and may be employable with a standard leaf electroscopes to produce a very-sensitive, low cost detector. The VUV source will ionize most molecules, while leaving air unionized, and the platinum catalyst source will generate positive ions in proportion to the concentration of vapour present. Increased sensitivity to low levels of formaldehyde and VOCs should be achievable by a number of methods such as: by adjusting the sensitivity of the electroscope; by adjusting the size of the source; and/or by measuring for longer periods. There should be ample room to modify the system to achieve the target levels of materials in indoor air.

Following the literature review, preliminary designs for several prototypes were to be formulated, then evaluated. Following the design review, prototypes were to be constructed and characterized following a well-defined test protocol.

The proposed low-cost, versatile detectors should be of interest to the homeowner, educator, home inspector and other individuals concerned with resolving indoor air quality problems.

2.0 SPECIFIC PROJECT OBJECTIVES

- To review the literature on methods of formaldehyde detection and to develop an annotated bibliography.
- To identify methods which offer promise for spot or rapid measurement at indoor air levels, particularly, those which can be incorporated into a portable instrument.
- To design and construct prototype detectors based on these technologies and to incorporate a common leaf electroscope as a readout device.
- To characterize the performance of these detectors. In particular, the sensitivity, the accuracy and efficiency, range, stability, reproducibility, linearity, humidity and temperature influence, ability to withstand the rigours of shipping, and the specificity of the prototypes for formaldehyde will be investigated.
- To evaluate the resulting information in terms of existing instruments and measurement methods.
- To reach conclusions on the success/failure of the project.
- To define strategies for improvement/modification of the prototypes.

3.0 PROTOTYPE ONE/PLATINUM CATALYST SOURCE

3.1 Background Description

Prototype one is presented in figures 1,2,3 and 4. The prototype consists of a platinum wire ion generator, an electroscope ion detector, supporting electrical and airflow systems, and a means for sampling VOCs and introducing samples into the electroscope.

The platinum wire ion generator, figure 1, is located in the electroscope, near the electroscope center electrode. The generator is connected to an external power supply capable of providing about 2.0 amperes of current in a controlled fashion. The ion generator produces positive ions in the presence of organic molecules when it is operated at a temperature of about 800 degrees centigrade, a temperature which corresponds to the stated current of 2.0 amperes. The positive ions so produced are measured by the simple leaf electroscope, and the rate or magnitude of deflection of the leaf is a measure of the ion production rate of the ion generator, or the number of organic molecules present.

Once the current to the ion generator is turned on, it must operate for a minimum 24 hours before measurements can be made, in order to burn off any VOCs or other materials which have been absorbed onto the surface of the platinum wire. These adsorbed materials produce ions and must be removed by heating. As burnoff proceeds, fewer ions are generated and the electroscope discharge time increases. A point is eventually reached where the discharge time reaches a constant value, usually longer than 10 minutes, and this time was employed for most experiments.

The ion generator is normally operated between 800 and 900 centigrade degrees during the burnoff period and is kept on continuously to prevent readsorption of materials.

The electroscope ion detector, figure 2, consists of a simple charged leaf electrode, mounted in a teflon insulator and enclosed in a glass housing, a means for charging the center electrode, and a means for reading out the angular deflection on a scale.

To make a measurement, the leaf electrode is first charged by means of an external charger, and a swivel arm momentarily contacts the leaf electrode in order to transfer the charge. The applied charge is negative and, enough charge is applied to deflect the leaf about 50 degrees. If a positive charge is applied, the electroscope does not discharge, probably because the ion generator does not produce negative ions in the presence of organic molecules.

The positive ions generated by the ion generator are immediately

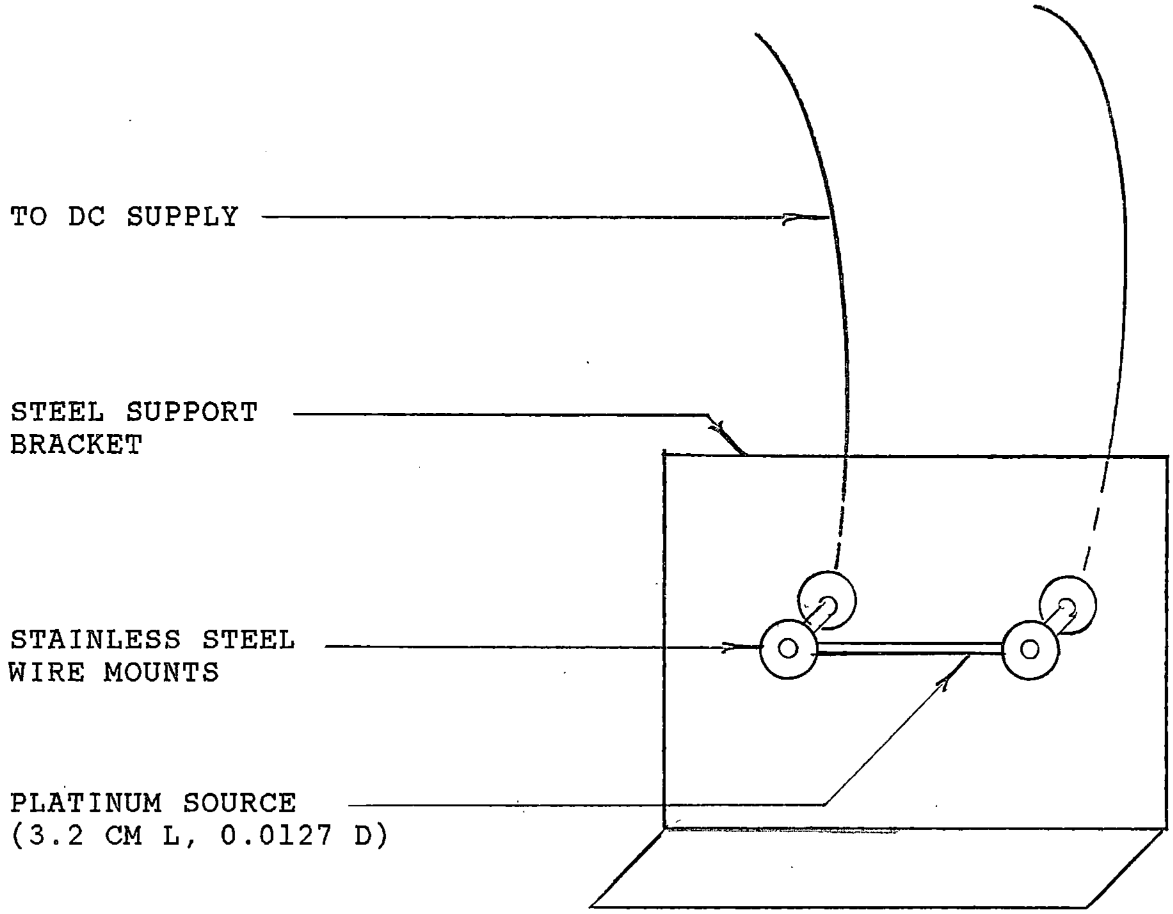


FIGURE 1 SIMPLIFIED PLATINUM WIRE POSITIVE ION GENERATOR

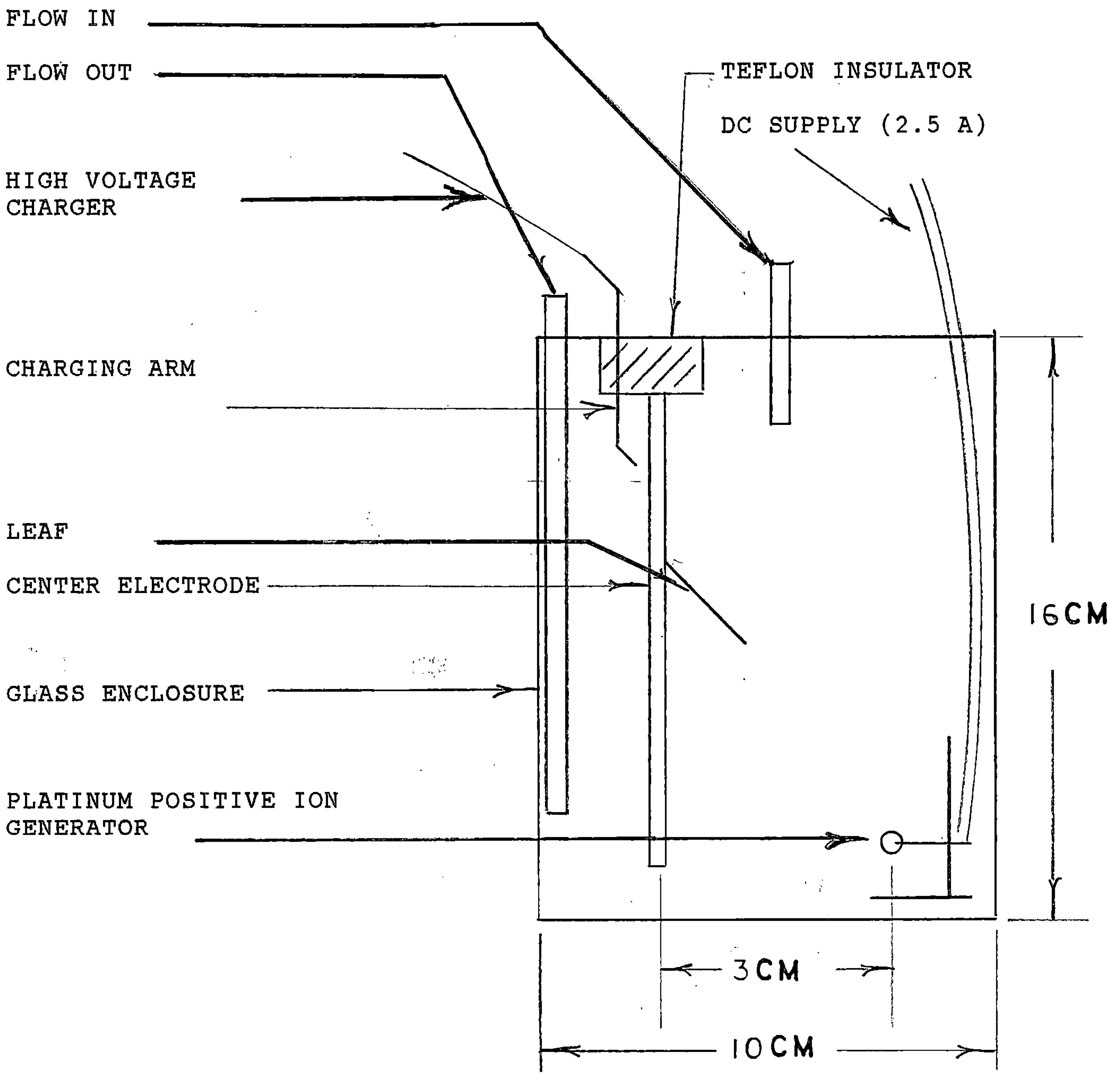


FIGURE 2 ELECTROSCOPE LAYOUT/PLATINUM POSITIVE ION SOURCE

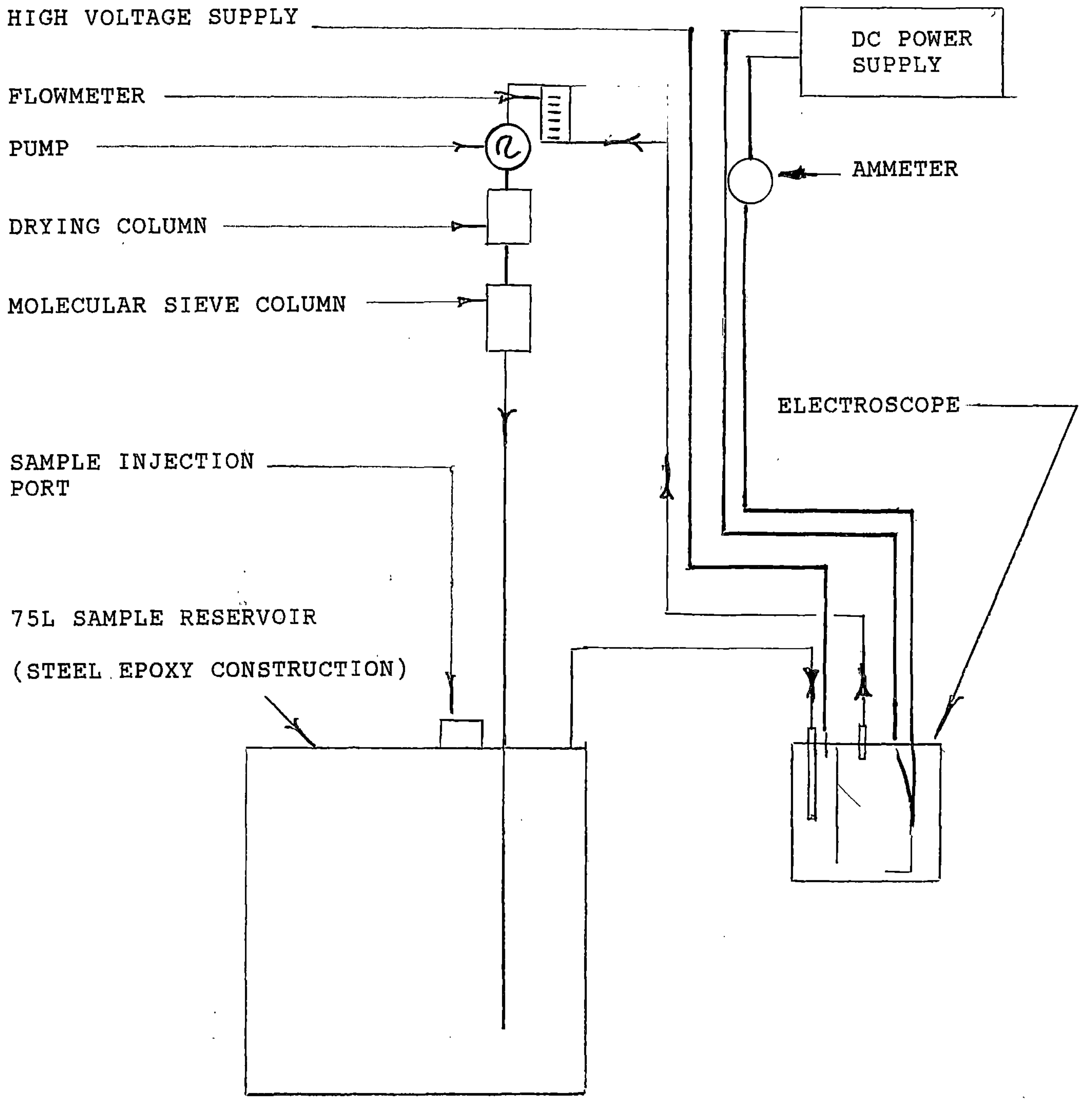
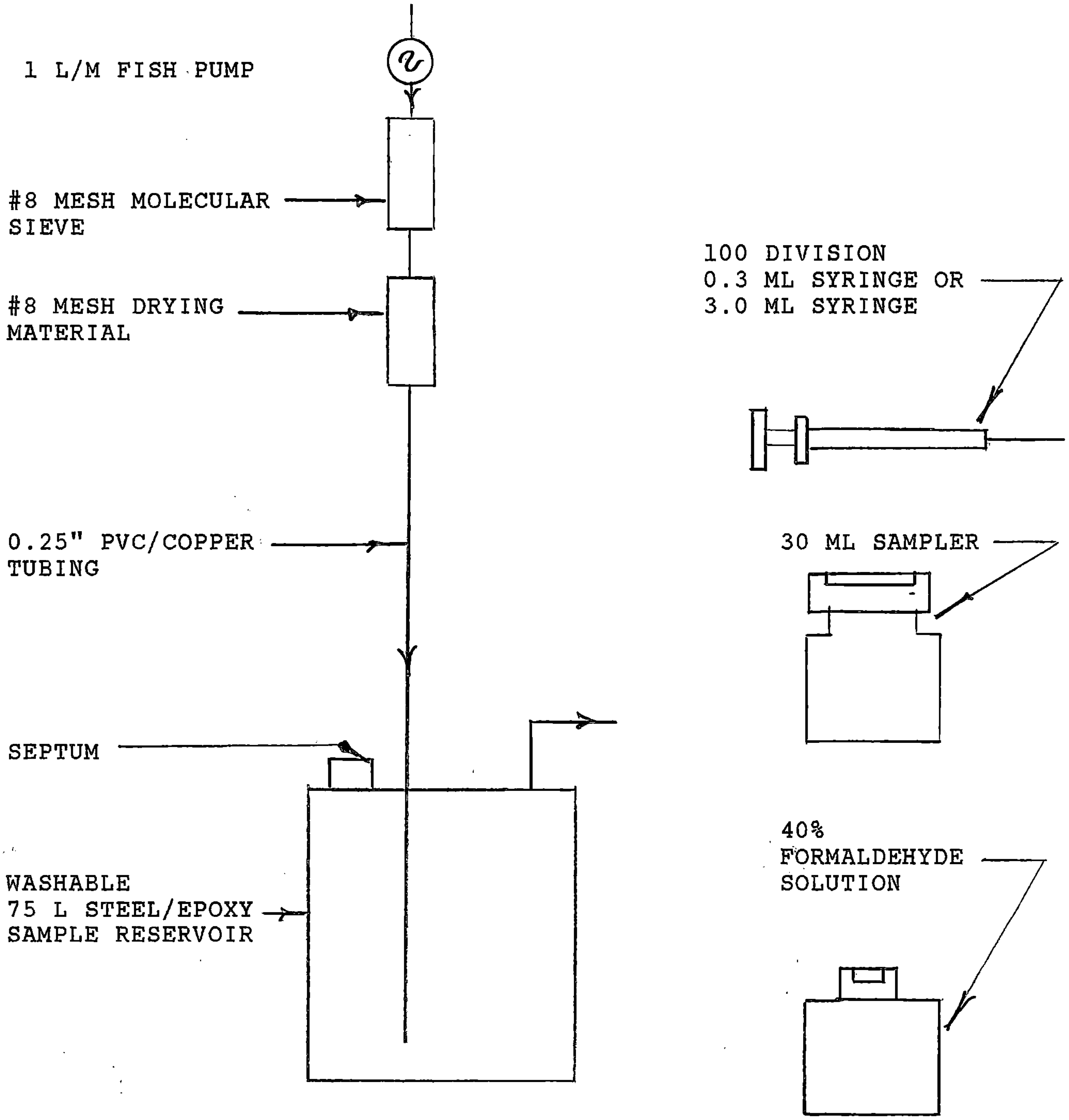


FIGURE 3 EXPERIMENTAL SETUP/PLATINUM WIRE SOURCE



SAMPLING METHOD
SAMPLE TAKEN FROM 40% FORMALDEHYDE SOLUTION WITH SYRINGE/DILUTED IN 30 ML SAMPLER IF NEEDED (<1 PPM), RESAMPLED WITH A 3 ML SYRINGE AND INJECTED INTO THE 75 L CONTAINER

FIGURE 4 SAMPLE INJECTION METHOD

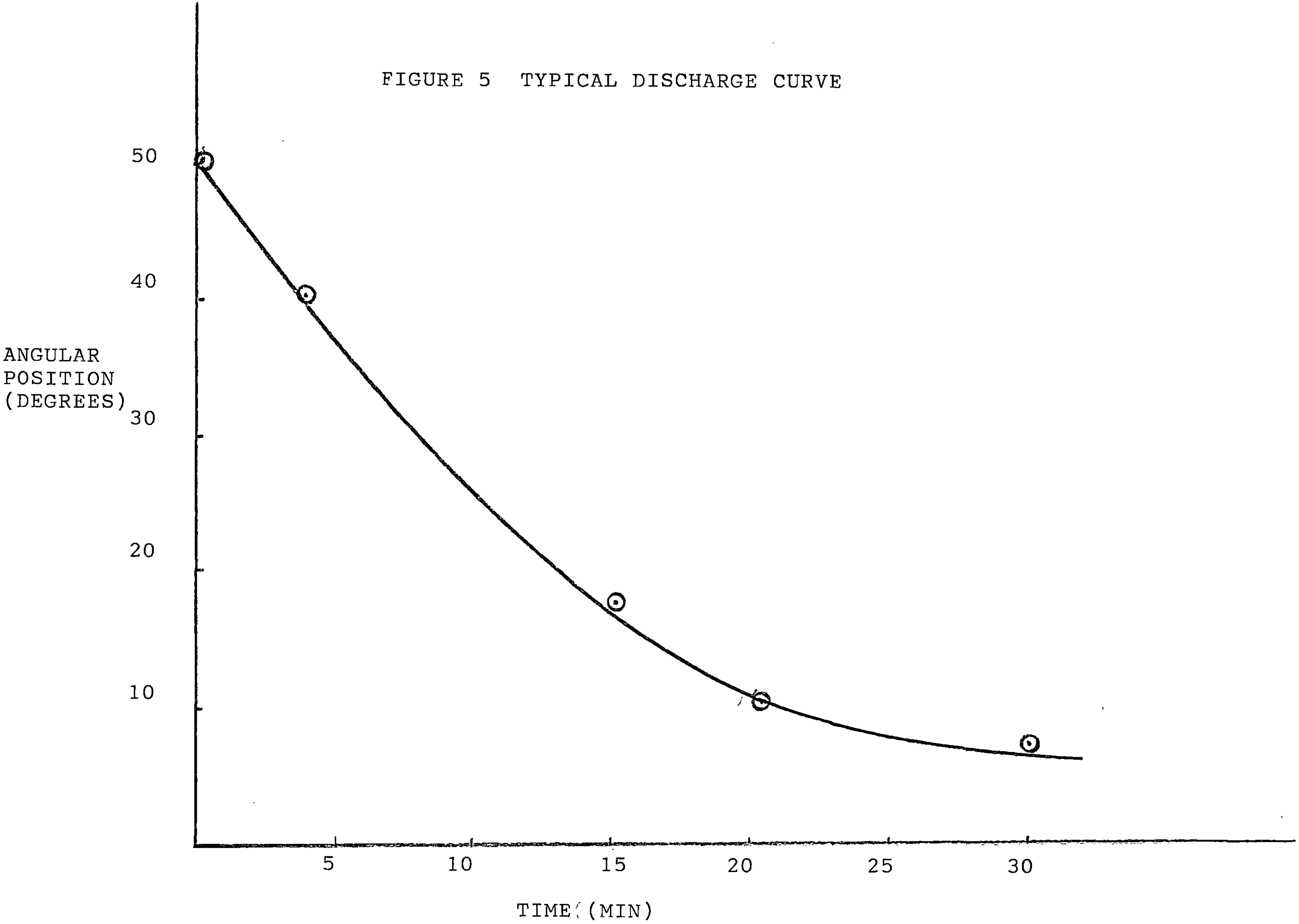


FIGURE 5 TYPICAL DISCHARGE CURVE

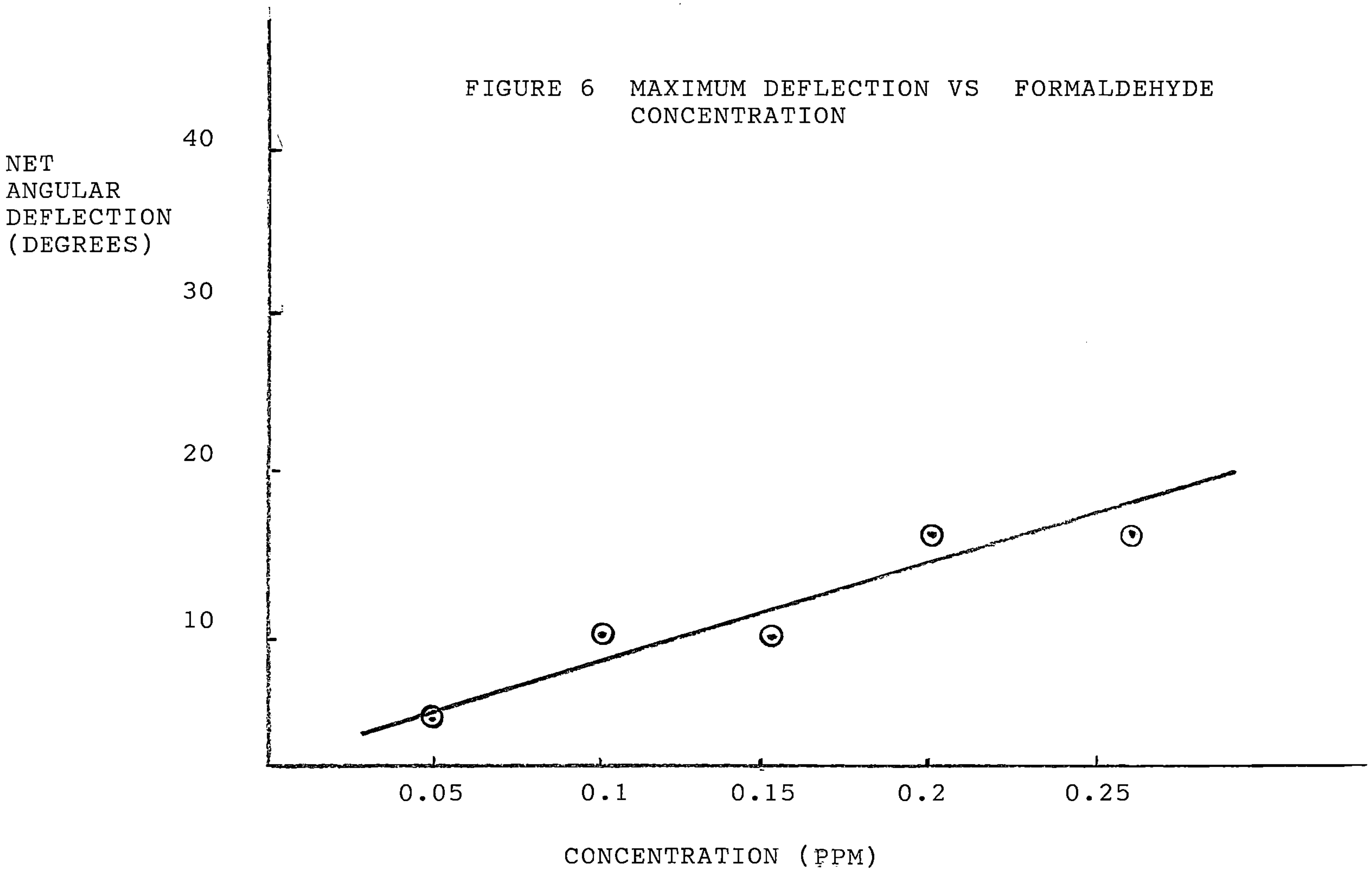


FIGURE 6 MAXIMUM DEFLECTION VS FORMALDEHYDE CONCENTRATION

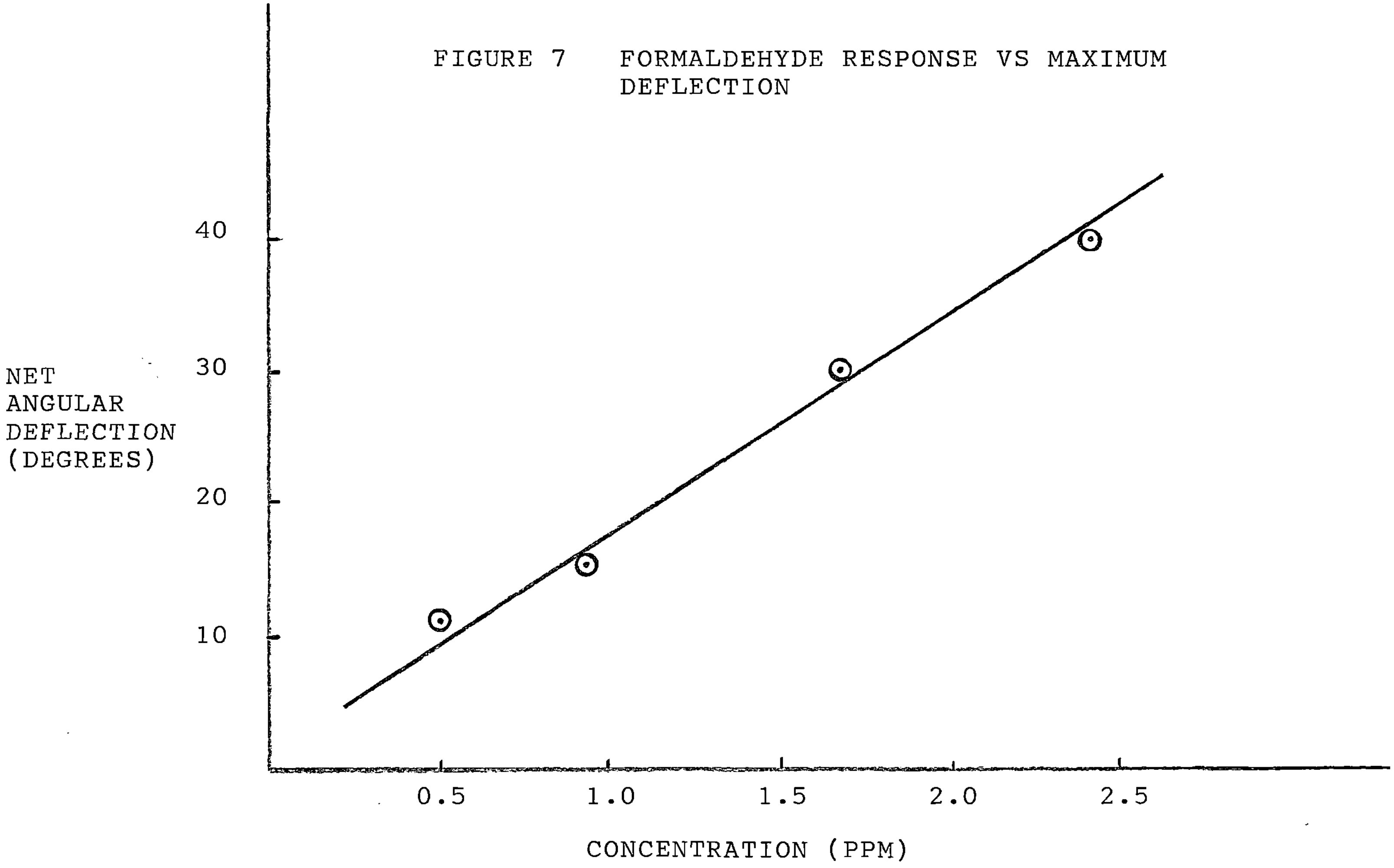
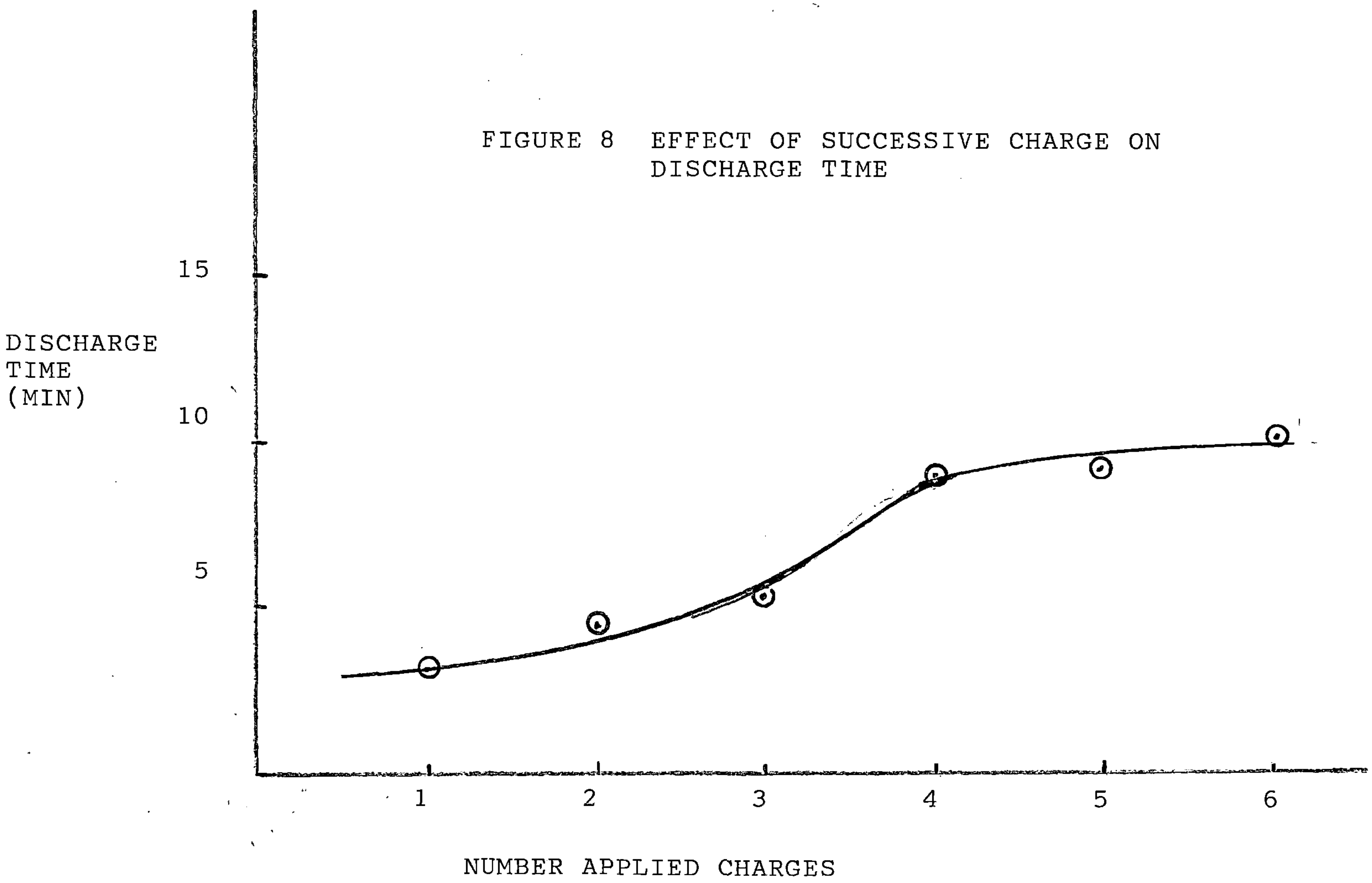


FIGURE 7 FORMALDEHYDE RESPONSE VS MAXIMUM DEFLECTION

FIGURE 8 EFFECT OF SUCCESSIVE CHARGE ON DISCHARGE TIME



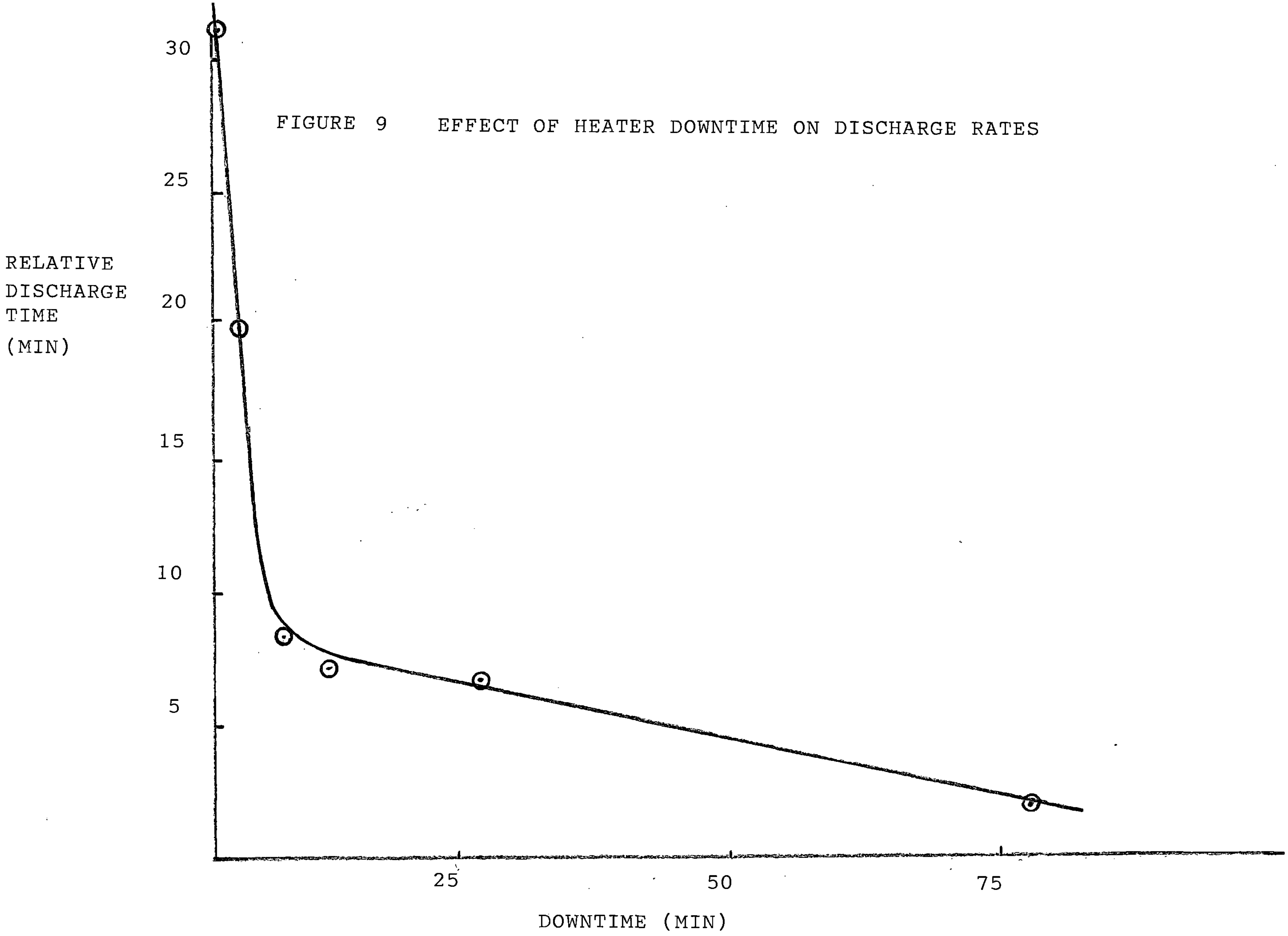


FIGURE 9 EFFECT OF HEATER DOWNTIME ON DISCHARGE RATES

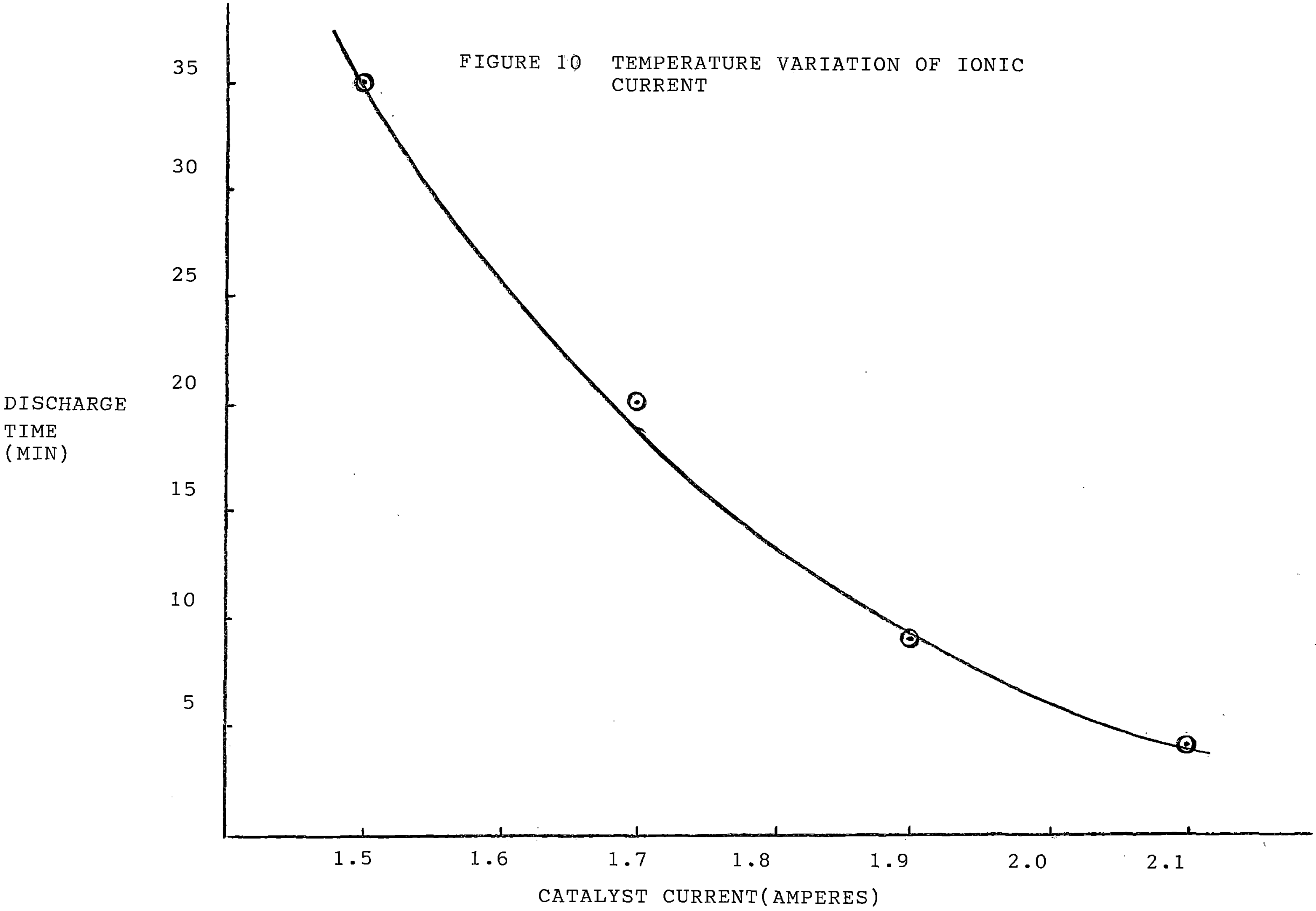
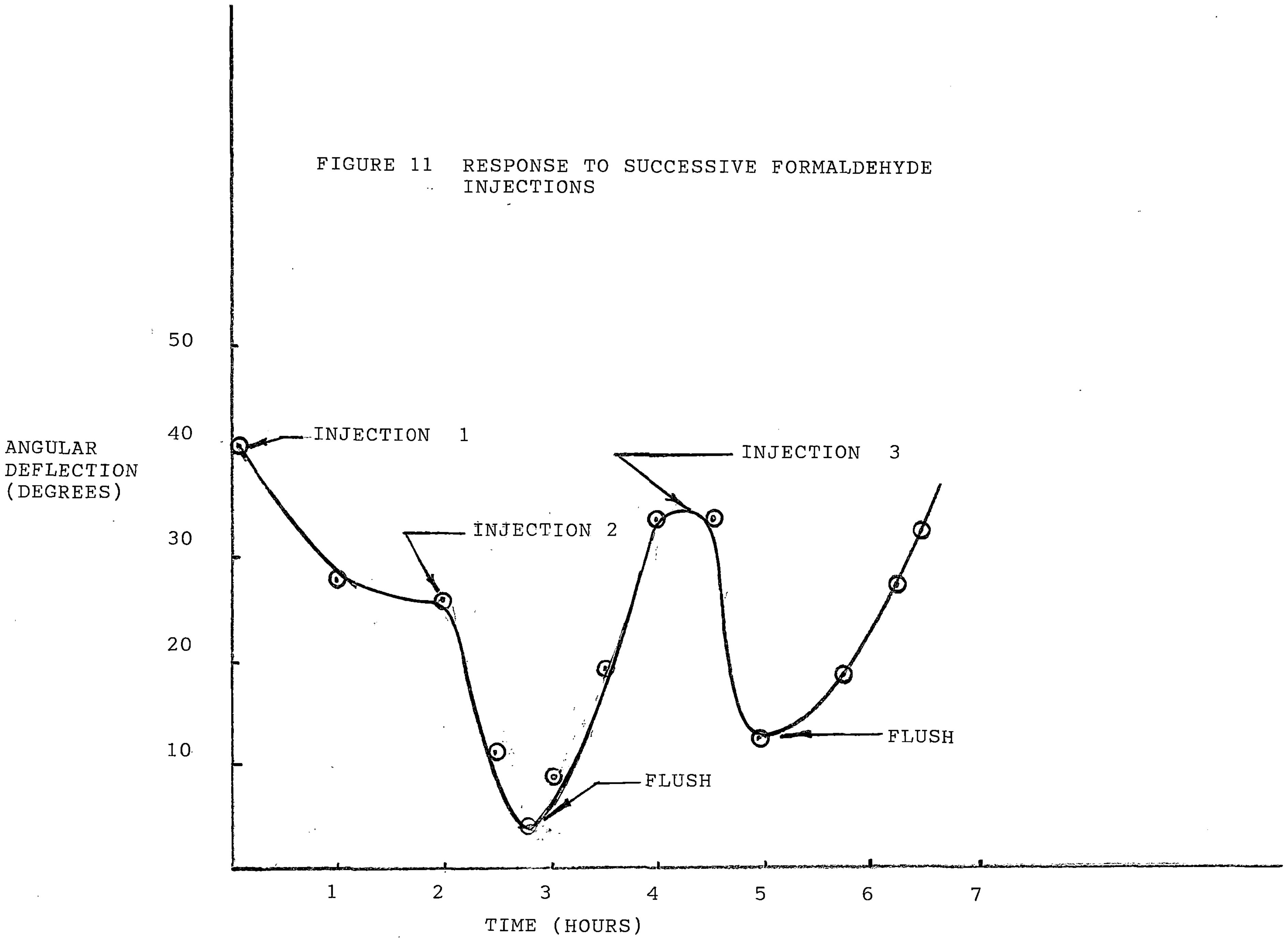


FIGURE 10 TEMPERATURE VARIATION OF IONIC CURRENT

FIGURE 11 RESPONSE TO SUCCESSIVE FORMALDEHYDE INJECTIONS



attracted to the center electrode where they start to neutralize the applied charge. As the charge is reduced on the center electrode, the deflection of the leaf changes. Since the process of ion generation and detection is a continuous process, the time to discharge the electroscope over a fixed deflection e.g. 50 to 15 degrees, was usually employed as a measure of the rate of ion production or, of the concentration of VOC present in the electroscope.

A voltage of 3000 volts, applied to the center electrode, will attract most of the charge generated by the ion generator. As the electroscope is discharged, the voltage drops, and some of the ionic charge produced by the ion generator, escapes. A chimney-effect, caused by the high temperature air around the platinum wire ion generator, tends to carry the charge away from the electroscope center electrode. At about 400 volts (15 degrees deflection) the amount of charge lost becomes significant, and this voltage or deflection was taken as the minimum operating voltage for the electroscope.

The sensitivity of the electroscope, defined as the leaf deflection per number of ions collected, must be matched to the ion generation rate of the ion generator in order to achieve a reasonable measurement period at a given concentration. If the ion generation rate at 0.01 parts per million of formaldehyde is too small for example, then the sensitivity of the electroscope must be high in order to achieve a discharge time between 10 and 40 minutes, times considered fast enough for efficient measurements. The sensitivity of the electroscope can be easily modified by changing its electrical capacitance or alternatively the ion production rate can be modified by various means such as by increasing power to the generator, and/or changing the wire dimensions.

Supporting electrical, airflow and sampling systems provide high voltage to the center electrode, power to the ion generator, and provide a means for introducing samples into the electroscope at specific concentrations. The airflow system is connected to a 75 dilution tank which is used to prepare samples at the desired concentration. Drying and molecular sieve columns are provided to treat the air in the 75 liter tank and, to remove residual humidity and the VOCs that are present. VOC residuals are difficult to remove in an unheated sampling system and tend to remain adsorbed on plastics and other materials. Considerable time is required to reduce the background from adsorbed VOCs to an acceptable level.

Additional aspects of the prototype detectors are discussed in more detail in sections i) to x) below.

i) Platinum catalyst ion generator

The platinum catalyst ion generator, presented in figure 1. is comprised of a 1.27 millimeter diameter platinum wire, 31.75 millimeters in length, and fixed in position between two porcelain insulated mounting posts. The posts are mounted on stainless steel brackets and the connecting wires are insulated by teflon sleeving.

In general, the source, when operated at about 2.0 amperes current, reached a temperature of about 800 C. The current was controlled to +/-0.01 amperes, since fluctuations larger than this had a marked effect on the electroscope discharge time i.e. performance.

ii) Electroscope

The electroscope is presented in figure 2. The electroscope was constructed of glass and stainless steel to minimize both corrosion and the adsorption/desorption of trace contaminants on exposed surfaces. Adsorbed vapours may be released into the electroscope at a later time, and in a manner which may interfere with measurements being made at that time. The released vapours therefore are an unwanted background and much of the time expended in making measurements focused on reducing this background to acceptable levels.

The central electrode was a stainless rod of 31.75 millimeters diameter. A stainless foil of 400 square millimeters was attached to the bottom of the central electrode to increase the electrical capacity. The center electrode was mounted on a teflon insulator, located at the top of the electroscope. The leaf was a light aluminum foil, hinged or fastened three quarters of the way up the electrode. The leaf deflection was read out from a simple angular scale located on the surface of the electroscope wall, and the leaf deflection was easily read with an accuracy of +/- 1 degree, in the range of deflection from 10 to 50 degrees.

The center electrode was charged by either a piezoelectric crystal or an electronic charger. To charge, the charger arm was rotated to touch the center electrode and rotated away to break the contact after charging. A voltage of -3000V was easily generated and, reliably produced a deflection of about 45 to 50 degrees. A negative charge was applied to the electrode in all experiments since there was no response when a positive charge was applied.

The electroscope grounded element was located external to the glass enclosure and was constructed of an aluminum foil. The electroscope sensitive volume was one liter.

The platinum ion generator was located at the bottom of the electroscope about 20 millimeters from the center electrode. The position was not optimized, since the extremely high ion currents noted at the stated position were an adequate starting point for the research. Deflection times of over 10 minutes were observed after a 24 hour burnoff time and the sensitivities of the electroscope and platinum ion generator appeared to be suitably matched.

With the platinum ion generator functioning, a noticeable chimney effect was observed, due to local heating around the ion generator. To minimize ion losses due to this effect, the center electrode voltage was always maintained above 400 volts.

Airflow lines into and out of the electroscope were 5.6 millimeter stainless or copper piping. One of the pipe connectors protruded to the bottom of the electroscope and the second connected near the top. This arrangement improved mixing before the sample contacted the platinum ion generator.

iii) Supporting electrical and sampling systems

The experimental setup is presented in figure 3 and, is comprised of an external dilution tank of 75 liters, a 50 gm drying column, a 50 gm molecular sieve column, a small 1 liter per minute fish pump, a flowmeter, a high voltage power supply, a DC power supply and an ammeter.

Stainless or copper tubing was employed where possible. Some difficulty was experienced with PVC tubing which tended to build up background quickly and as a consequence had to be frequently replaced. New PVC tubing emitted vapours for considerable time, a fact which caused considerable delay since the tubing had to be purged for a long period before use.

The 75 L reservoir contained a sample injection port, and samples were injected via a syringe or micropipette directly into the chamber or onto a filter which was inserted into the chamber. In some cases, the sample had to be gently heated. Concentrations from 0.01 to 2.5 ppm were easily achieved with this setup.

The high voltage supply was permanently connected to the electroscope charging arm and turned on only as required. Either a simple piezoelectric crystal or an electronic supply was employed. The crystal contacts of the piezoelectric device were reversed to provide a negative charge to the center electrode. The electronic supply was developed in a previous project. In all cases a reproducible voltage of about -3000V was easily achieved. Provision was made for adjusting the leaf arm position and an alpha particle source was employed for this purpose.

The variable DC supply was capable of supplying up to 2.5 amperes continuously to the platinum ion generator. The supply had to be accurately monitored to +/- 0.01 ampere since variations larger than this tended to affect the discharge time.

iv) Means for sampling VOCs

The test apparatus is presented in figure 4. The standard equipment consisted of a 75 liter dilution chamber, a 100 division 0.3 ml syringe, a 30 ml dilution bottle, 100 ul micropipets calibrated in ul, and solutions of 40% formaldehyde and purified acetone.

In practice an appropriate volume of either formaldehyde or acetone was taken with either the micropipette or the syringe and injected into the 75 liter chamber. The sample was then gently heated if necessary to vaporize any liquid residue. The pump was then turned on and air was circulated at a rate of about 0.5 L/min from the sample chamber into the electroscope. The air stream after leaving the electroscope was then either recirculated back into the sample container or vented to the outside. In some cases, the drying and molecular sieve columns were removed to explore the effects of humidified air on the response of the system. Occasionally, the flow rate was altered.

Levels of 0.01 to 2.5 ppm were easily established with the setup. These levels were not verified by an independent method however, and the materials employed were assumed to be reasonably pure.

Plastics and drying or molecular sieve materials tended to develop backgrounds after exposure to organic vapours and where possible metals or glass were employed. Otherwise the plastics were replaced frequently. New PVC tubing can, introduce a significant background and must be purged for lengthy periods before use.

In those situations where the backgound persisted after replacement of the external sampling lines, the sampling volume which consisted of the tubing, the air pump, the electroscope, and the 75 liter dilution tank, were continuously purged through molecular sieve columns until an acceptable background was achieved.

3.2 RESULTS

3.2.1 Factors Which Affect Performance

The construction materials, electric charge applied to the electroscope center electrode, airflow through the electroscope, ambient temperature and humidity, separation of the platinum wire from the electroscope center electrode, platinum wire dimensions, method of charging the electroscope, source off time, temperature of the platinum wire, and electroscope discharge characteristics, are all factors which can affect performance and were therefore investigated experimentally.

i) Construction materials

This work focused on defining suitable construction materials to employ in the electroscope, airflow and sampling systems. Materials tend to adsorb vapours at the trace level and rerelease them after exposure. If the target sensitivities for the organic samples being measured are low, then the rereleased vapours may interfere with the measurements.

PVC tubing and other plastic materials tended to absorb organic vapours on exposure and then slowly release them. This effect resulted in an undesirable background which was reduced only after lengthy pumping (days) or removal of the tubing or material.

Similarly, drying materials and sieves also contributed to the background after absorbing organic materials and then slowly rereleasing them to the air flowing into the electroscope. As a consequence, these materials were changed frequently in order to keep background levels low.

As a result of early experiments on construction materials, glass, teflon, copper or stainless were employed where possible. In addition, materials were cleaned by washing with methanol and/or boiling in distilled water prior to use.

The adsorption of materials on surfaces may be reduced, and the rate of desorption of the adsorbed materials increased, by heating the surfaces or the whole system to 100 degrees centigrade or more. This method of managing background was not investigated since time was not available.

None of the components in the electroscope deteriorated during the lengthy test period of about 4 months, although the platinum positive ion source was operated continuously at about 800 C during this time. The high temperature corrosive atmosphere present in the electroscope did not appear to affect performance, even though a deposit slowly formed in and around the insulator on the electroscope center electrode.

Surprisingly, the electroscope performed well at elevated relative humidities, even though electrical leakage from the center electrode and across the insulator to ground, should be large and have had a significant impact on performance at elevated humidities. This surprising result may be due to the fact that the insulator is continuously heated by the platinum wire and, as a result, kept dry enough to minimize leakage.

ii) Electric charge applied to the electroscope center electrode

This work focused on establishing, the useful operating voltage range of the electroscope, the correct voltage polarity (negative or positive) to apply, and characteristic discharge times to expect. The performance of the ion generator was also investigated.

The electroscope deflected about 45 degrees upon application of a negative or positive voltage of 3000 V to the electroscope center electrode, and discharged at a rate of about 5 degrees per day with the ion generator off and no sample present. The discharge rate was slightly higher than the value expected from background gamma radiation (1 liter volume electroscope) but, was low enough for this research project, since discharge times in typical experiments were around 1 degree per minute.

No significant response was observed for positive applied voltages with the platinum ion generator running and a sample present. The conclusion must be that no negative ions are produced by the platinum ion generator in the presence of organic materials.

With a negative applied voltage, the electroscope discharged instantaneously in clean air with the platinum ion generator running. Positive ions were thus being produced by the ion generator, while it burned away organic contaminants present on the platinum wire. The contaminants were often materials adsorbed from the air onto the wire, or transferred to it by touching.

The positive ion current decreased as the contaminant was burned away, and as a consequence the time for the electroscope to discharge increased. At 2.00 amperes applied current, maintained for about 24 hours, the time to discharge the electroscope slowly increased to about 30 minutes in the absence of a sample.

A voltage of -3000V was applied to the center electrode in all studies, unless otherwise stated. This applied voltage corresponded to a leaf deflection of about 45 degrees. The electroscope discharged between 45 and 15 degrees in a linear fashion (range used) and some non linearity was observed below 15 degrees (figure 5). Below 15 degrees the center electrode voltage of -400 volts was inadequate to attract all of the positive ion current from the platinum ion generator and some of the ions were carried away by the chimney effect. The range of linear response was thus 30 degrees, a range corresponding to a discharge time between 10 and 30 minutes.

iii) Airflow through the electroscope

The airflow through the electroscope may affect performance (electroscope discharge time) by, a) changing the temperature of the platinum wire which in turn affects the positive ion current, b) influencing the chimney effect which tends to carry ions away from the center electrode, c) changing the degree of mixing and the distribution of the sample within the electroscope.

No appreciable change in the discharge time was observed for air flows in the range from zero to 1 liter per minute, with the ion generator on and no sample present. A standard airflow rate of 0.5 liters per minute was employed for most experiments unless otherwise stated.

When a sample of formaldehyde is present, the electroscope discharge time decreases as the airflow is increased and care must be taken to maintain a constant airflow rate in all experiments. One or more of the factors mentioned, such as mixing, may provide an explanation for the dependence of discharge time on airflow rate, but the relationship is unclear.

One possible explanation, is that the formaldehyde sample is being removed from the air by some process, such as adsorption, and in order to achieve the maximum concentration of sample in the electroscope, the sample must be moved from the dilution tank to the electroscope as rapidly as possible. The fastest discharge times were observed at the highest flow rates.

iv) Ambient temperature and humidity

In this section the influence of ambient temperature and humidity on the electroscope discharge rates was evaluated.

The rate of discharge of the electroscope in the absence of a sample was relatively constant (1 degree/min) over the temperature range from 10 to 35 centigrade degrees. The high platinum wire temperature of about 800 C, and the temperature of the interior of the electroscope remained relatively constant with changes in the ambient temperature and, consequently, so did the rate of ion production by the ion generator or the rate of discharge of the electroscope.

The rate of discharge of the electroscope in the absence of a sample was relatively constant for humidities between 20 to 90%. Outside air (clean air) was employed in these studies, cleaned with sieves, then humidified and pumped through the electroscope.

For most studies the ambient temperature was about 20 C and the ambient humidity ranged from 50 to 90 % relative humidity. Since these conditions are well within the limits of testing reported above, humidity and temperature are not expected to have a significant influence on the results of other experiments.

It should be noted that the outside air employed in these studies initially passed through PVC tubing, which was subsequently replaced by copper tubing, because excessive levels of contaminants were being released by the PVC tubing into the air sample.

v) Separation of the platinum wire from the electroscope center electrode

In this section, the effect of separation of the platinum ion generator and the electroscope center electrode on the electroscope discharge time was examined. Discharge times would be affected (lengthened) if some of the ions generated by the ion generator were not collected efficiently by the electroscope center electrode. There is a competition between ion collection, as a result of the center electrode high voltage, and ion loss, which is due to a chimney effect and to the random loss of ions on walls and surfaces in the interior of the electroscope.

The electroscope discharge rate is constant over the range of discharge voltages from -3000V to -400 V (figure 5) and for distances of separation ranging from 5 millimeters to 30 millimeters. Below -400 V the discharge rate slows and becomes nonlinear. At this voltage ion collection becomes less efficient since the force of attraction for the positive ions is being effectively countered by the convective airflow (chimney effect) due to the hot platinum ion generator.

As a consequence of these experiments, a distance of separation of 30 millimeters between the electroscope center electrode and the platinum ion generator, and an operating voltage range between -3000 volts and -400 volts for the electroscope center electrode, were adopted in subsequent experiments.

vi) Platinum ion generator wire dimensions

In this section the influence of the wire diameter and length on the ion generation rate were examined. Since ion production is defined in terms of ion emission per unit of area, increasing the wire length or diameter should both increase ion emission, provided the process is not limited by a lack of organic molecules or carbon deposits on the wire. Increasing the wire diameter or length quickly increases the power requirements at a constant temperature, and in a portable device, there is an optimum tradeoff point between the various factors.
Increasing the ion production rate results in increased

sensitivity, and is one means for improving performance.

As expected, doubling the length of the platinum wire from 30 millimeters to 60 millimeters, doubled the ion production rate as determined by monitoring the discharge rate of the electroscope. The effect of wire diameter on ion generation rates was not studied.

Since a wire diameter of 0.127 millimeters and a wire length of 30 millimeters resulted in reasonable electroscope discharge times for organic vapour concentrations ranging from 0.01 parts per million to 2.5 parts per million (see figures 6 and 7), the ion generator in subsequent experiments was constructed from a wire of these dimensions.

vii) Method of charging the electroscope

In this section the performance of the electroscope as related to its previous state of charge, is examined. It has been reported in the literature on a number of occasions that the ability of an electroscope to retain its state of charge is related to its previous charge history. Previous electroscopes had to be recharged a number of times in succession, or maintained in a charged state and not allowed to discharge for any length of time, before the electrode would retain the applied charge in a reproducible manner. This behaviour was previously attributed to phenomena such as dielectric relaxation or insulator polarization (soaking).

In this research, the discharge time of the electroscope was significantly affected by the number of times it was charged until it reached a charge plateau (figure 8). Thus, after the electroscope was left discharged for a significant period (several hours) in the open atmosphere, it had to be charged repeatedly until the discharge rate reached a constant value. Once the electroscope reached this plateau, it discharged in a reproducible manner.

Although the literature attributed this behaviour to dielectric soaking, the result may also be due to the random collection of ions on the insulator during the electroscope off period. Certainly, when the ion generator is also turned off the effect of dielectric soakage is much less pronounced. No attempt was made to investigate this behaviour, although simple shielding of the insulator from the ions present in the hot convective air stream, may eliminate the problem.

viii) Ion generator off time

In this section the effect of turning off the ion generator on the recovery of the system to its prior operating point was investigated. This is an important factor, since portable instruments are normally turned off until a measurement is made. Any delay in reaching a reproducible operating point after turn on will seriously affect its usefulness.

While the ion generator is turned off, it may adsorb organic materials present in the ambient air. These materials must be burned off before the ion generator can return to its normal operating point. During the burn-off period positive ions are produced which discharge the electroscope and the rate of discharge should be a measure of the positive ion current, the amount of material adsorbed and/or the off time of the positive ion generator.

Results presented in figure 9 demonstrate this effect and, the electroscope discharge time varies inversely with ion generator off time, although the relationship is non linear. The most rapid changes occur during the first five minutes and the discharge time drops from 30 minutes to about 6 minutes during this period. After about 75 minutes, the electroscope will discharge in seconds. For an ion generator off period of one day the discharge rate is instantaneous.

Once power is applied to the platinum ion generator, adsorbed material begins to burn off and, the electroscope discharge time starts to increase until it reaches a constant value which is proportional to the platinum wire temperature.

The adsorbed materials seem to be adsorbed in proportion to the exposure time and possibly in proportion to the concentration of the organic vapour present, although the later possibility has not been thoroughly studied. Once the ion generator is turned on positive ions are generated until the material is burned away. This interesting result suggests that simple platinum wires may be employed as ambient air samplers for trace level measurement. The platinum wire would be left exposed for a period, then heated. The magnitude of the discharge may be proportional to the trace level concentration.

ix) Dependence of ionic current on temperature

In this section the effect of temperature on the ionic current was studied. The ionic current from the platinum ion generator is related to the amount of organic vapour present and to the current passing through the wire (temperature). Since the discharge time of the electroscope is related inversely to the ionic current, then an optimum operating temperature must be sought which is a balance between the operating temperature of the ion generator, the sensitivity of the device to organic vapours and, a discharge time which is of convenient length. In this section a convenient measurement time was taken as between 10 and 40 minutes. The relationship between discharge times and operating temperature was derived for adsorbed substances rather than for organic vapours.

The experimental relationship between the electroscope discharge time and the ion generator current (temperature) is presented in figure 10. As expected, the electroscope discharge time varies inversely with the current applied to the ion source. At 2.0 amperes applied current, the temperature of the platinum ion generator was about 800 degrees centigrade.

As the source temperature increases, the discharge time decreases dramatically due to increased ion production by the ion generator. At a given current level, however, the discharge time gradually increases until it reaches a constant value of 30 to 40 minutes (2.0 amperes), a value which is dependent on the purity of the ambient air.

At increased ion generator temperatures, increased ion production thus appears to increase sensitivity. An upper limit to the operating temperature is set by the melting point of the wire, the sensitivity needed to detect VOCs at 0.01 parts par million, the power requirements, and the electroscope discharge time considered to be convenient (<40 minutes). A current of 2.0 amperes was employed in all experimental work and there was no need to vary this current in order to improve performance.

x) Electroscope Discharge Characteristics

In this section, the discharge characteristics of the electroscope such as, linearity, reproducibility, useful operating range and, sensitivity were examined.

A typical discharge curve for the electroscope (2.00 Amperes) is presented in figure 5. The curve is linear in the range of 45 to 15 degrees and becomes slightly non linear below 15 degrees. The 45 to 15 degree range was chosen as the operating range for most experiments and the time to discharge over this range was a measure of the ionic current generated by the ion generator. The non linear discharge rate at low angular deflections (voltages <400 V) was probably due to incomplete collection of ionic charge. Some of the ions were probably carried away from the center electrode by convection currents generated by the hot platinum ion generator.

The discharge time of the electroscope was about 30 minutes at 2.0 amperes current to the ion generator. There were no problems in reading the electroscope at this slow discharge rate and a reproducibility of +/- 1 degree was achieved.

Experiments with formaldehyde and acetone confirmed that the experimental setup was sensitive enough to measure these vapours down to 0.03 ppm or less. The overall sensitivity of the device is related, to the sensitivity of the electroscope, the characteristics of the ion generator such as wire length or diameter and applied power, to the distance of separation of the ion generator and the electroscope, and to characteristics of the vapour being measured. Although it was possible to increase the sensitivity of the device, to measure below 0.01 parts per million, adsorption becomes a significant problem, particularly in an unheated system, and this research objective was not explored at this time.

3.2.2 Response of Prototype to Formaldehyde

In this section the performance of the prototype as a formaldehyde detector is presented. The reproducibility of measurement, minimum detectable level, linearity, range, accuracy, stability and susceptibility to interferences were established.

Results are presented in figures 6,7 and 11.

The response of the prototype to three successive injection and purge sequences is presented in figure 11. Each injection of formaldehyde was equivalent to a concentration of 0.8 parts per million and resulted in maximum deflections of 14 degrees (Generator current=2.00 A, Flow=0.5 L/min). After each minima the system was flushed and a sample was introduced. The response of the system was slow and about thirty minutes was required for the electroscope discharge time to reach a minimum deflection. Several hours of flushing were required before the electroscope discharge time returned to normal and another sample could be introduced. Faster response times are probably achievable with increased flow rates or by heating the system and, both approaches should facilitate quicker removal of formaldehyde residuals.

In figures 6 and 7, the response of the system in the concentration range from 0 to 2.5 ppm is presented. At lower formaldehyde concentrations (figure 6), the source current was increased from 2.0 to 2.10 amperes and the platinum wire length was increased from 30 to 60 millimeters to increase the sensitivity above standard conditions. In both cases the response was linear over the ranges considered and a minimum detectable level of 0.01 parts per million was achieved.

i) Reproducibility

This is a function of many variables (flow and mixing, formaldehyde volatilization rates, ion generator current, timing, readout error and electroscope sensitivity, construction materials employed, sample accuracy)

Successive injections at the 0.5 ppm formaldehyde level resulted in deflections of 13, 11, 8 and 16 degrees and, successive injections at the 1.6 ppm level produced deflections of 24, 36, 30 degrees. The reproducibility estimated from these measurements is +/- 15% to 20%.

With improvements in sampling techniques and better control on other factors, measurement reproducibility could be improved. The results are promising at the present time and demonstrate that the factors which affect performance are being controlled.

ii) The minimum detectable level

The minimum level detectable must be below 0.05 parts per million, the Health and Welfare Canada long term exposure level for residential housing, for the prototype to be useful for most routine indoor air quality investigations in residences. No commercially available instruments have achieved this level of sensitivity.

A minimum detectable level of 0.01 ppm was achieved with the prototype described above (figure 6). The level can be lowered by increasing the sensitivity of the prototype and by improving sampling techniques, but below 0.01 ppm, difficulties are experienced in purging sample residuals. As a result, the time between measurements is excessively long. In a more sophisticated design, heating would improve performance.

The lower limit of detection is set by such factors as the background, factors affecting reproducibility, timing, readout error, materials employed, distance of separation of the ion generator and electroscope, the electroscope sensitivity, and the applied voltage.

iii) Linearity

Linearity is defined as a straight line response between the sample concentration and the electroscope discharge time. Many factors such as wire temperature, wire surface area, electroscope linearity, applied voltage, readout error, and sampling error must be well defined and managed to prevent nonlinear behaviour.

For the carefully controlled experiments presented in figures 6 and 7, the response was determined to be linear in the concentration range from 0.01 to 2.5 ppm.

iv) Range

The range of response defines the useful range of concentrations and electroscope discharge times over which the performance of the prototype can be reliably used.

The response was found to be linear over the concentration range from 0.01 parts per million to 2.5 parts per million. With care, concentrations below 0.01 ppm should be readily measured by changing factors that affect sensitivity such as, the surface area of the platinum source and/or the power to the source. The range should be extendable above 2.5 ppm by changing factors such as ion generator power, increasing the surface area of the platinum wire ion generator and by reducing the sensitivity of the electroscope.

v) Accuracy

Measurement accuracy usually is defined as the ability of the prototype to measure some reference concentration of formaldehyde and is expressed as the standard deviation of the mean. Permeation tubes or calibrated reference detectors can be used to establish a standard reference concentration. These methods were considered beyond the scope of this research project and an uncalibrated formaldehyde solution (40% v/v) was employed for intercomparison purposes. Based on this solution, the estimated accuracy is +/-15 to 20%.

vi) Stability

The prototype must measure formaldehyde reliably, in a reproducible manner, without any drift, and many factors, particularly the ion generator current, must be carefully controlled to achieve reliable results.

The platinum ion generator and electroscope did not deteriorate during the test period although there was some evidence of corrosion on the teflon insulator. The graphical information presented in figures 6 and 7 was obtained at widely spaced intervals over the measurement period.

Further work is needed to establish the long term performance of these detectors.

vii) Interferences

The research focused initially on the development of a detector which would measure formaldehyde and would not respond to other organic vapours. The specificity of the detector was determined by evaluating its response to acetone, a typical VOC.

The deflection was found to be similar for formaldehyde and acetone (30 degrees at 1.6 ppm). The rate of discharge and cleanout times were much different for the two VOCs, however, suggesting that the prototype may be made more specific by investigating timing patterns.

Since the prototype was found to respond to VOCs, including formaldehyde, it is a TVOC (total volatile organic carbons) detector. In fact, the prototype probably responds directly to the carbon content of the molecules being measured, and is an extremely sensitive and true gauge of the TVOC content of the ambient air.

Time was not available to investigate methods for making the detector more slective in reponse.

3.2.3 Response to Acetone/VOCs

In this section, the response of the prototype detector to acetone was determined using the same experimental techniques as for formaldehyde. Acetone volatilized more quickly than did formaldehyde and was easier to purge from the prototype detector.

The response at 1.6 ppm was measured and deflections of 31, 24 and 19 degrees were observed. The magnitude of the response is similar to that for formaldehyde and there does not appear to be any way of distinguishing the two VOCs on the basis of their sensitivity. As mentioned in a previous section, timing information may provide a useful means of distinguishing VOCs, but this approach was not investigated.

No VOCs other than formaldehyde and acetone were investigated in this project.

4.0 PROTOTYPE TWO-VUV BASED SOURCE

4.1 Background Description

The prototype detector is presented in figures 12 to 15. The detector is comprised of an electroscope, a Vacuum Ultraviolet (VUV) light source, and a sampling system.

The VUV source is designed to produce ultraviolet light over a broad spectrum from less than 50 nanometers to up to 200 nanometers in wavelength. Many organic molecules, including formaldehyde, will be ionized by this light but, unlike a radioactive source, the air will be left unionized. Thus, when organic molecules are irradiated by VUV light, a cloud of ions will be produced, the magnitude of which will depend on the concentration and volume of the organic molecules present, the intensity and energy of the VUV light and, on the type of organic molecule. The magnitude of the ion cloud can be determined by means of a charge measuring device such as an electroscope, where the rate of deflection of a foil leaf will provide an indication of the charge present and/or the concentration of the organic species being ionized.

The VUV source is a corona type discharge in a flowing argon gas flow. High voltage between two metal electrodes ionizes the pure argon gas present in the source enclosure. When the ionized argon molecules reacquire lost electrons, VUV light is emitted. The light is readily absorbed by many organic molecules and a special optical window of lithium or calcium fluoride must be employed to transmit light between the VUV source and the electroscope readout device, where the organic vapour is present.

The electroscope ion detector, figure 12, consists of a simple charged leaf electrode, mounted in a teflon insulator and enclosed in a metal housing, a means for charging the center electrode, a means for reading out the angular deflection on a scale, a means for sample introduction and, a window which transmits VUV light.

To make a measurement the leaf electrode is first charged by means of an external charger and, a swivel arm momentarily contacts the leaf electrode in order to transfer the charge. The applied charge is negative and, enough charge is applied to deflect the leaf about 50 degrees, as read from the scale mounted next to the optical viewing window.

The positive ions generated by the VUV light are immediately attracted to the center electrode where they neutralize the applied charge. As the charge is reduced on the center electrode, the deflection of the leaf changes and the magnitude or rate of deflection provides a measure of the number of ions produced by the generator and, the concentration of VOCs present in the electroscope. Since the process of ion generation and detection is a continuous process, the time to discharge the electroscope a fixed deflection e.g. 50 to 15 degrees, was usually employed to gauge the concentration of the VOC present in the electroscope.

The sensitivity of the electroscope, defined as the leaf deflection per number of ions collected, must be matched to the ion generation rate of the ion generator in order to achieve a reasonable measurement period at a given concentration. If the ion generation rate at 0.01 parts per million of formaldehyde is too small for example, then the sensitivity of the electroscope must be high, to achieve a reasonable discharge time i.e. 10 to 40 minutes. The sensitivity of the electroscope can be modified by changing its electrical capacitance or, alternatively, the ion production rate can be modified by increasing power, and changing the wire dimensions.

Supporting electrical, airflow and sampling systems provide high voltage to the center electrode, argon gas to the VUV ion source, and provide a means for introducing samples into the electroscope. The airflow system is connected to a 75 dilution tank which is used to prepare samples at the desired concentration. Drying and molecular sieve columns are provided to treat the air in the 75 liter tank, and to remove residual humidity and VOCs that are present in the system. VOC residuals are difficult to remove from an unheated sampling system and tend to remain adsorbed on plastics and other materials. They constitute a chemical backgound and considerable time is required to reduce the background to an acceptable level.

The argon gas supply consists of a tank, a regulator to control pressure and flow, a flowmeter to measure flow and, a valve. Gas flows of several milliliters per minute were sufficient to keep the atmosphere in the VUV source clean, thereby ensuring a useful light output from the source.

i) Electroscope

If a hinged leaf is electrically charged, the electric force will cause the leaf to be deflected from its uncharged vertical position. As the electroscope discharges, the leaf angle changes, the rate and/or magnitude of change being proportional to the charge generated in the electroscope sensitive volume. If any charge is present in the sensitive volume of the electroscope, the charge is quickly attracted to the center electrode where it neutralizes some of the charge which has been applied by the piezoelectric charger.

The leaf is constructed from an small piece of aluminum foil, and hinged to the center electrode. The center electrode is screw mounted to a teflon insulator which is held in place by the internal card guides of the aluminum box, used to house the electroscope. The airspace enclosed by the aluminum box and, from which ions are attracted to the center electrode, is termed the sensitive volume of the detector.

The leaf position is viewed through a transparent plastic window and the angle of deflection read from a scale (degrees) which is mounted on one side of the window. A second window on the opposite side of the electroscope provides backlighting.

The shape of the grounded area immediately around the leaf was optimized using shims to improve repeatability and charge linearity.

A sealed insulated contact is located near the leaf center electrode for charging purposes. The piezoelectric charger is housed on the top of the electroscope box. The position of the piezoelectric charging pin in relation to the center electrode established the amount of charge applied and, therefore, the angle of deflection of the leaf. The piezoelectric charger provided a very simple, low cost means of charging the electroscope.

Once charged, the angle of deflection is adjustable by means of an Am-241 alpha particle source which is located external to the box. Radiation from the source ionized the air inside the electroscope sensitive volume and, slowly discharged the electroscope until the desired angle of deflection was reached. An alpha transparent window was employed. The source was mounted on a swivel and could be moved away from the window to an off position when not in use.

The 15 millimeter diameter lithium fluoride VUV optical window was enclosed between teflon sheets and sealed to the lid of the electroscope.

The viewing and optical windows were electrically shielded by means of fine stainless steel mesh stretched across the windows and grounded to the aluminum housing, to prevent charge buildup.

The electroscope was sealed to prevent contaminant entry. Samples were introduced through two bulkhead air flow connectors; one acted as an inlet and the second as an outlet. Alternatively, these connectors could be capped and, the electroscope was operated without airflow. A small quantity of drierite was placed inside the electroscope to ensure low humidity under static and flow through conditions.

Care was taken in the construction of the electroscope to employ materials such as aluminum, stainless and teflon which were resistant to the VUV light. Joints, where sealing materials such as epoxy were employed, were kept well away from the VUV radiation to prevent deterioration, and the possible emission of contaminants (volatile organic carbons-VOCs) which would interfere with the measurements.

ii) VUV Source

A drawing of the source is presented in figure 13.

A corona discharge is generated by applying a high voltage to a small wire located near a ground element. The resulting discharge will generate VUV light, the intensity and spectrum of which is dependent on such factors as electrical intensity (wire diameter), source geometry, the nature and purity of the surrounding argon gas, and the gas pressure. The effectiveness of the VUV generated depends on the characteristics of the optical window and the discharge geometry. In this research argon gas was employed in a flow though arrangement at atmospheric pressure. The window material was lithium fluoride. The corona discharge was located close to the window to facilitate the transfer of as much of the VUV light produced as possible though the window and into the electroscope.

In practice, the argon tank was opened and the argon flow was usually adjusted to about 20 milliliters per minute. Flow conditions were found to be critical to the performance of the source and some research focused on defining the optimum conditions to employ. The corona discharge is affected by impurities present in the argon gas or impurities generated by interaction of light and heat with the materials comprising the source. Increasing the argon flow tended to reduce impurity levels and to improve the quality of the light produced.

The corona source generated and transmitted VUV light in the wavelength range from 50 to 200 nanometers. The higher energy components of the radiation exceeded the 10.8 electron volts needed to ionize formaldehyde and most other organic molecules, but did not ionize air molecules. As a consequence, only ions generated by ionizing organic molecules present in the sensitive volume of the electroscope, contribute to the discharge of the electroscope.

The corona source was easily and cheaply constructed.
The source consisted of a fine wire which was located between two parallel rods. The rods and wire were mounted on a printed circuit board. The board in turn was supported by a bracket and held in place by the card guides of the aluminum box used to house the source. The design of these various supports allowed the position of the corona discharge relative to the VUV exit window to be varied and the location to be optimized. In addition, the corona discharge characteristics could be optimized by moving the rods relative to the fine wire.

Construction materials were selected for their resistance to VUV light and for their low emission characteristics. Since one of the objectives of the current research was to develop a simple low cost technology, commonly available materials and simple construction techniques were employed as much as possible.

The high voltage leads were fed through the source housing by means of two sealed banana jack connectors. Inlet and outlet gases were fed through two bulkhead connectors.

The electroscope with its VUV transparent window (lithium fluoride) was sealed to the source housing, once the performance and optimization of the electroscope was complete. This fragile window deteriorated slowly with exposure to humidity and VUV light but no obvious changes in transmission properties of the window were noted over the four month test period. The window is the most expensive component of the prototype detector and no low cost alternative methods of transmitting VUV light were found.

The high voltage supply used with the VUV source was one previously developed at InstruScience Ltd. for charging the electroscope. It was a variable (2200 to 4400 Volts DC) high voltage supply with low power consumption (<200 Mw) and incorporated a custom made transformer with associated circuitry. For this research project, the supply was powered by a variable low voltage DC supply which allowed adjustment of the high voltage over a limited range.

A tank of Zero-Grade Argon gas, with two control valves was employed for most studies. Either valve could be used to turn the gas flow on or off while the second functioned as a safety valve. Between the second control valve and a flowmeter, a needle valve was used to adjust the air flow. After the flowmeter, the gas entered the VUV source through its bulkhead airflow connector and, in turn, exited via the second bulkhead airflow connector into the ambient air.

Copper tubing (0.25") was employed where possible to reduce contaminant buildup and adsorption.

iii) Sampling and airflow systems

A simple AC pump was used to supply air to the electroscope. In general, copper tubing was used where possible and, depending on the particular experiment, various drierite and/or molecular sieves traps (4-8 mesh) were added to dry and clean the air. The electroscope bulkhead air flow connectors were used for air inlet and outlet purposes. In some experiments, room air, or outdoor air was dried before passage through the electroscope in a flow-through arrangement. In other experiments, a molecular sieve trap was employed and the air was recirculated from the electroscope through either a 75 litre tank (sampling), or associated small volume, back into the electroscope.

FIGURE 12 ELECTROSCOPE

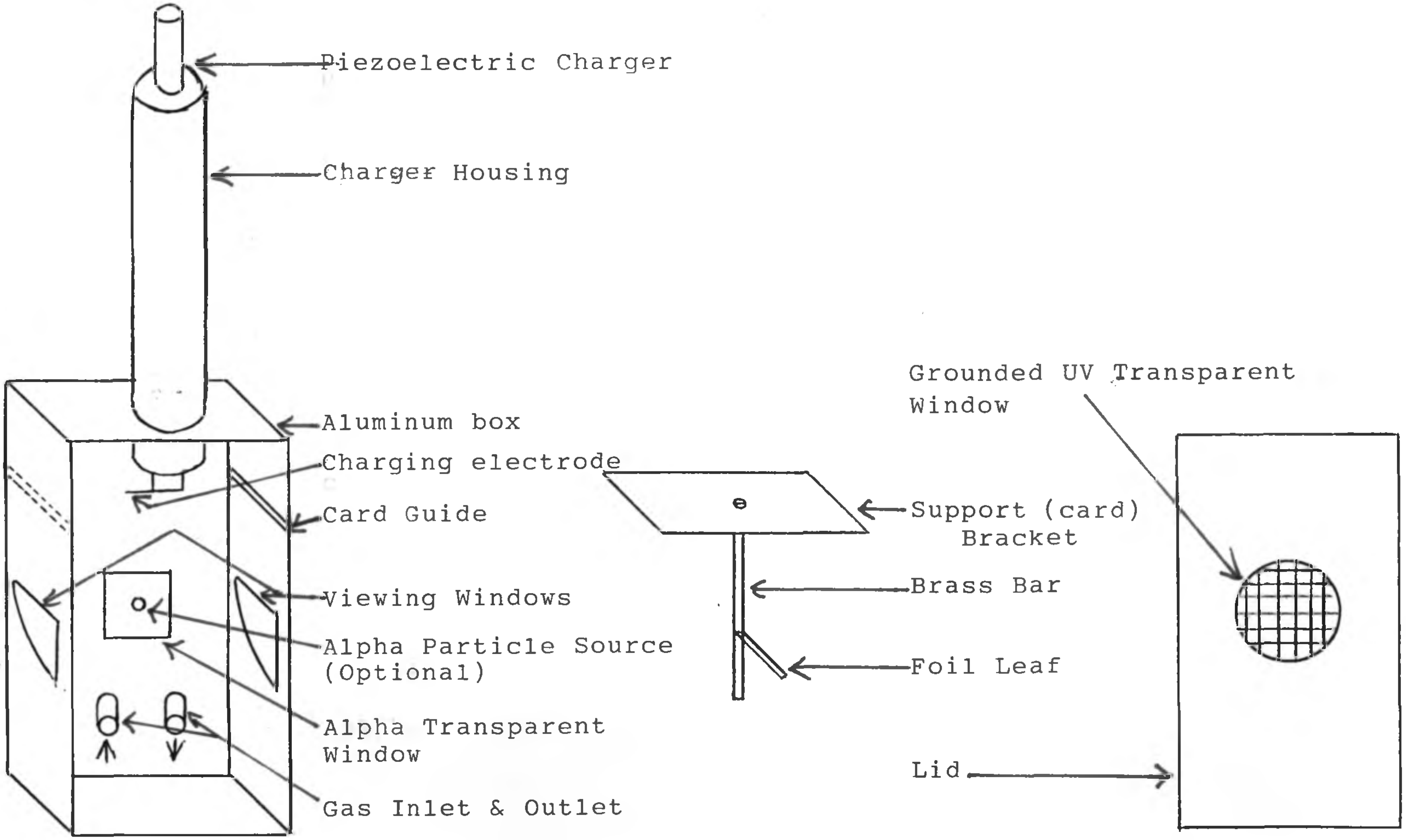


FIGURE 13 ULTRAVIOLET SOURCE

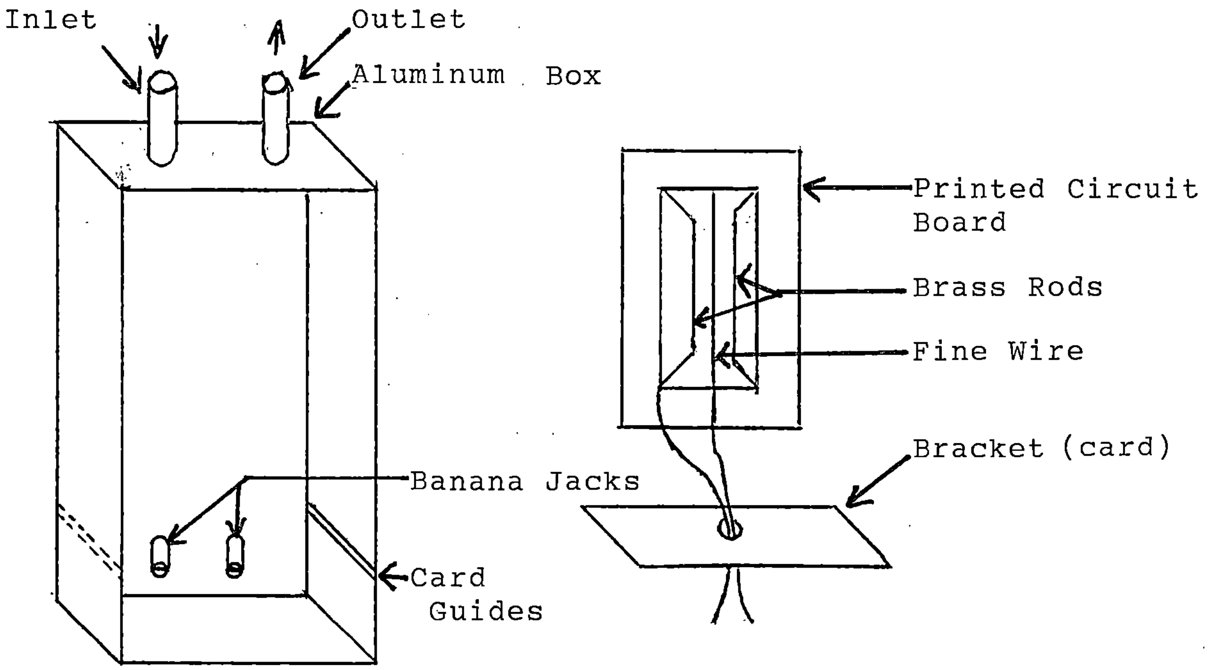


FIGURE 14 ARGON SUPPLY

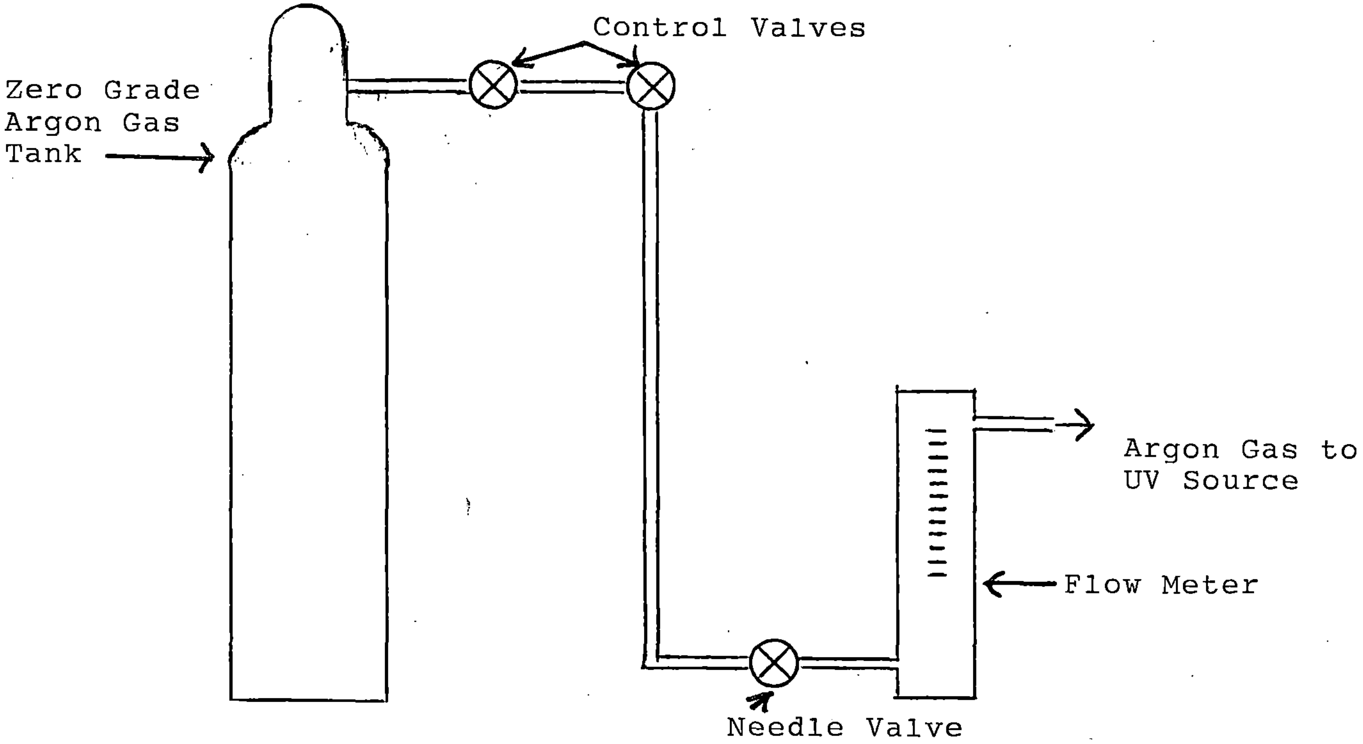


FIGURE 15 ELECTROSCOPE AIR SUPPLY

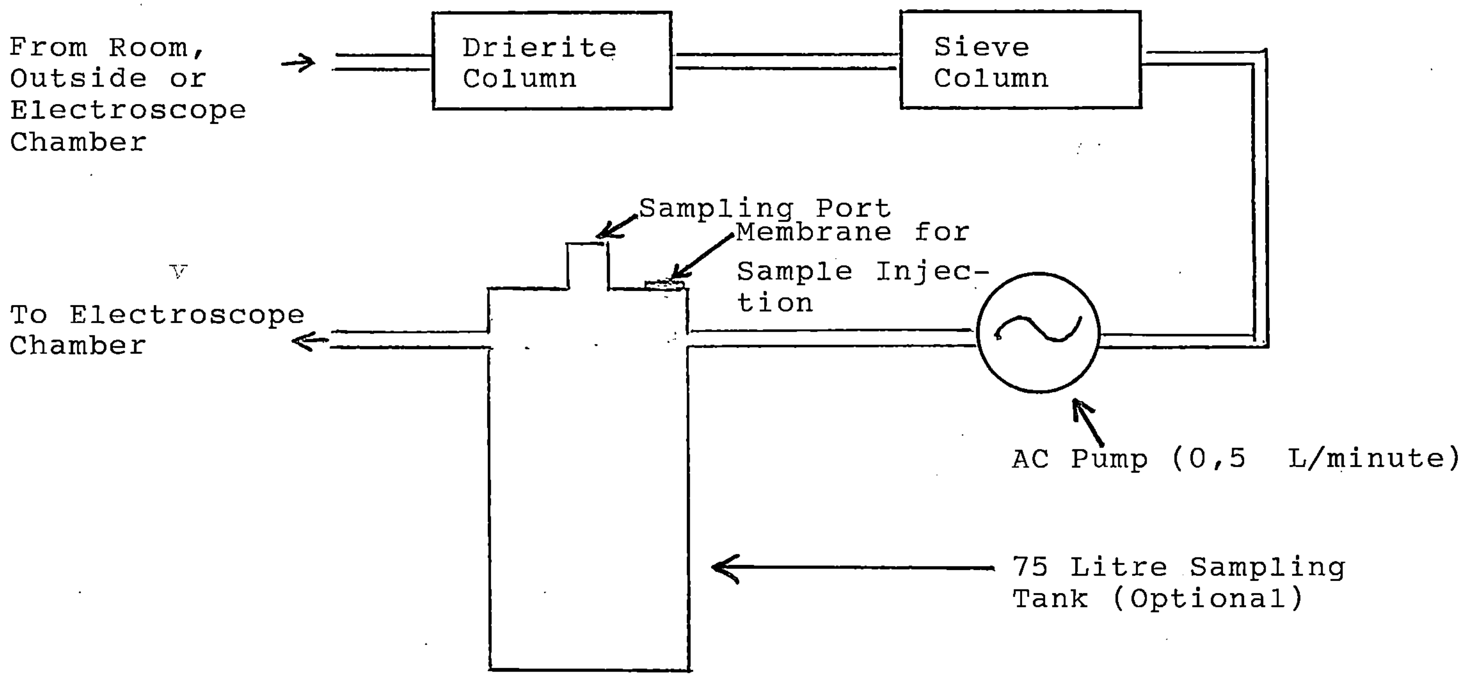


FIGURE 16 ELECTROSCOPE LINEARITY

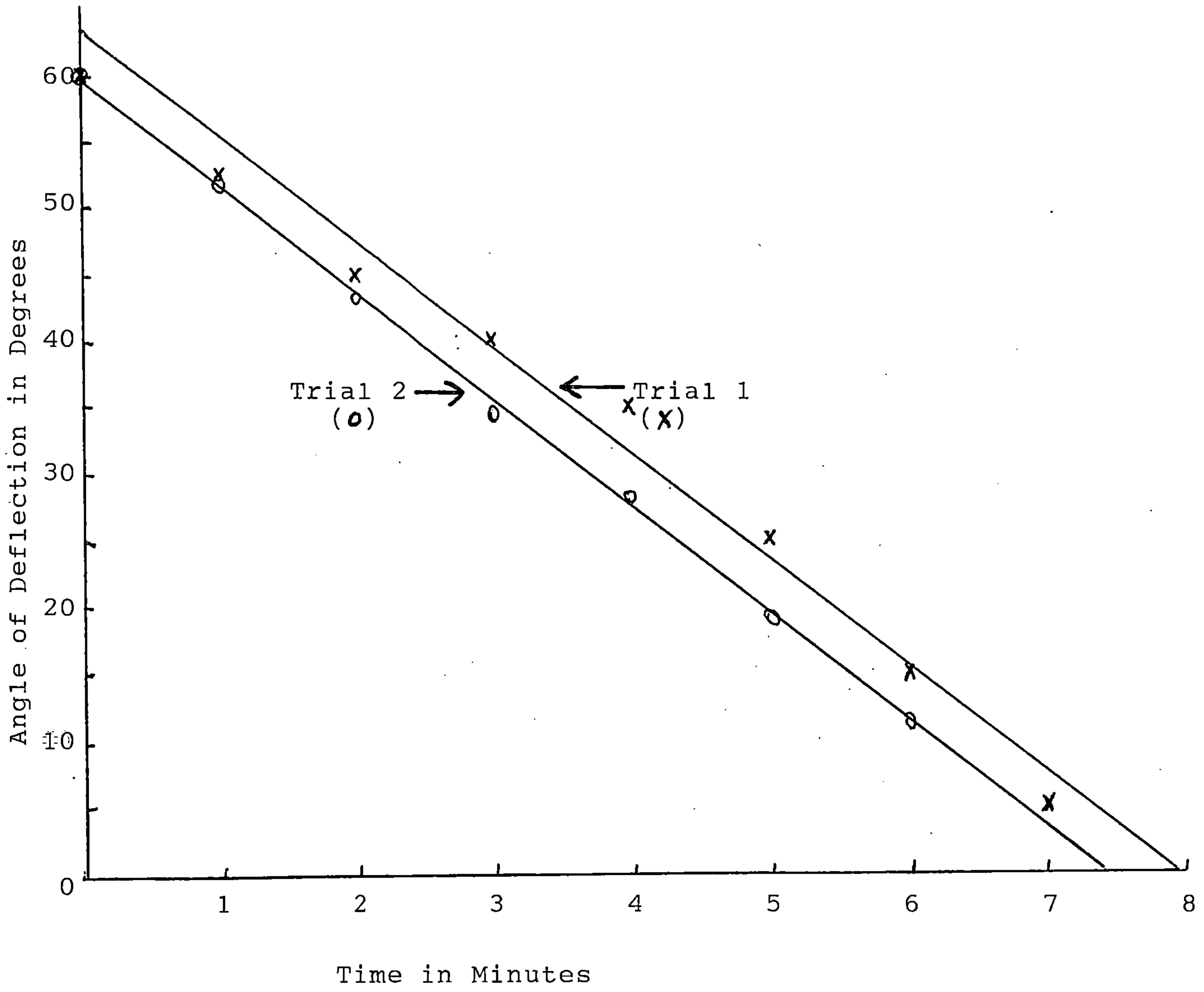


FIGURE 17 ARGON GAS FLOW EFFECTS

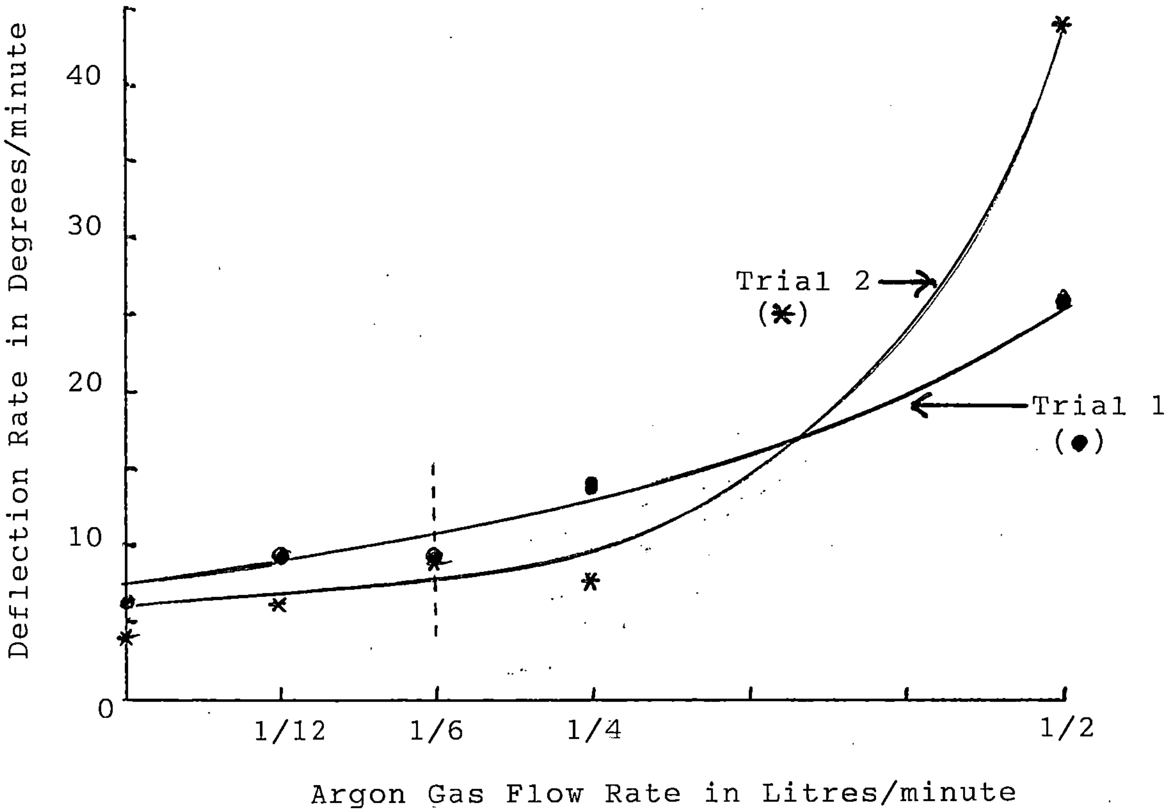


FIGURE 18 Acetone Concentration vs. Deflection Rate

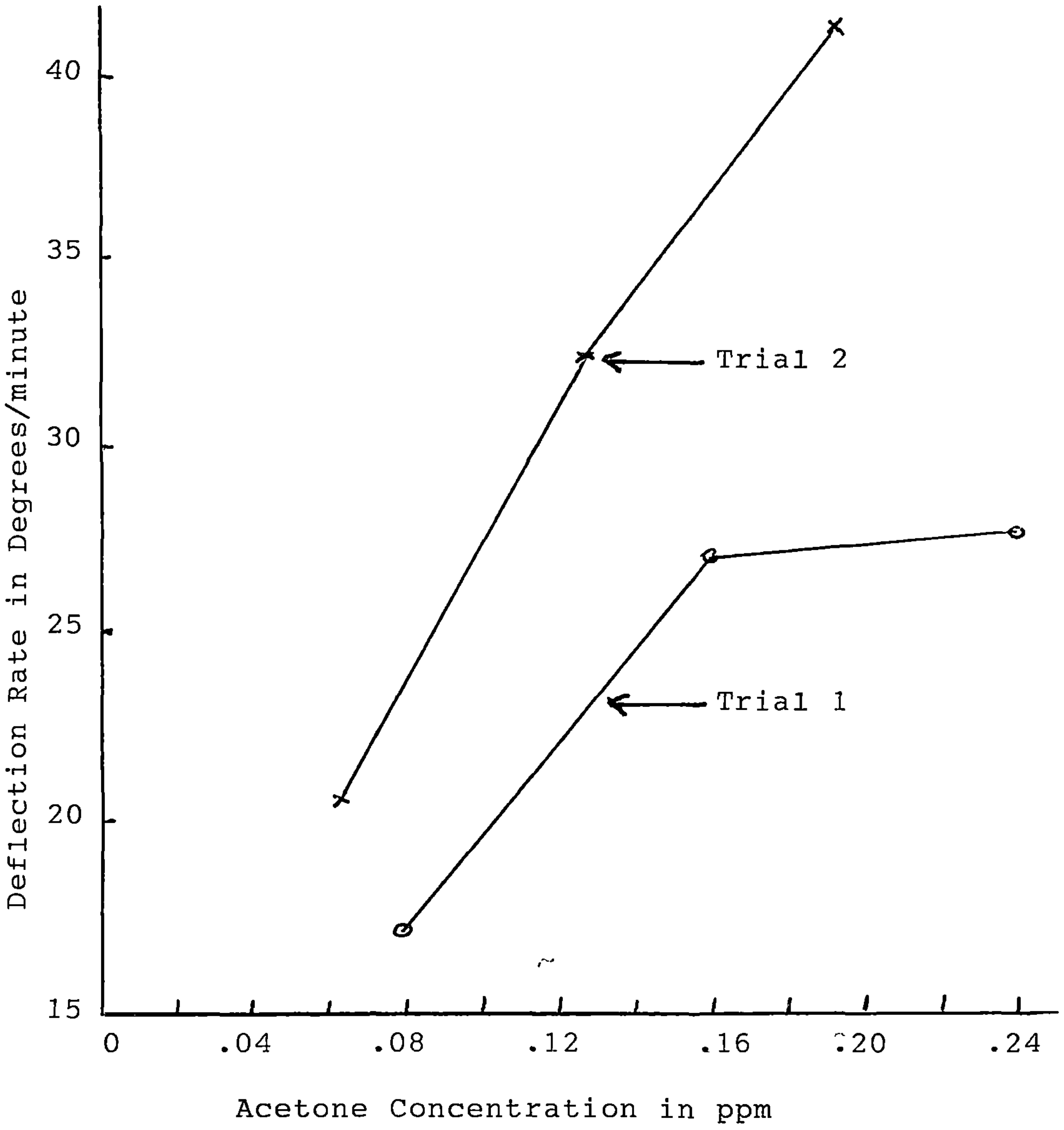
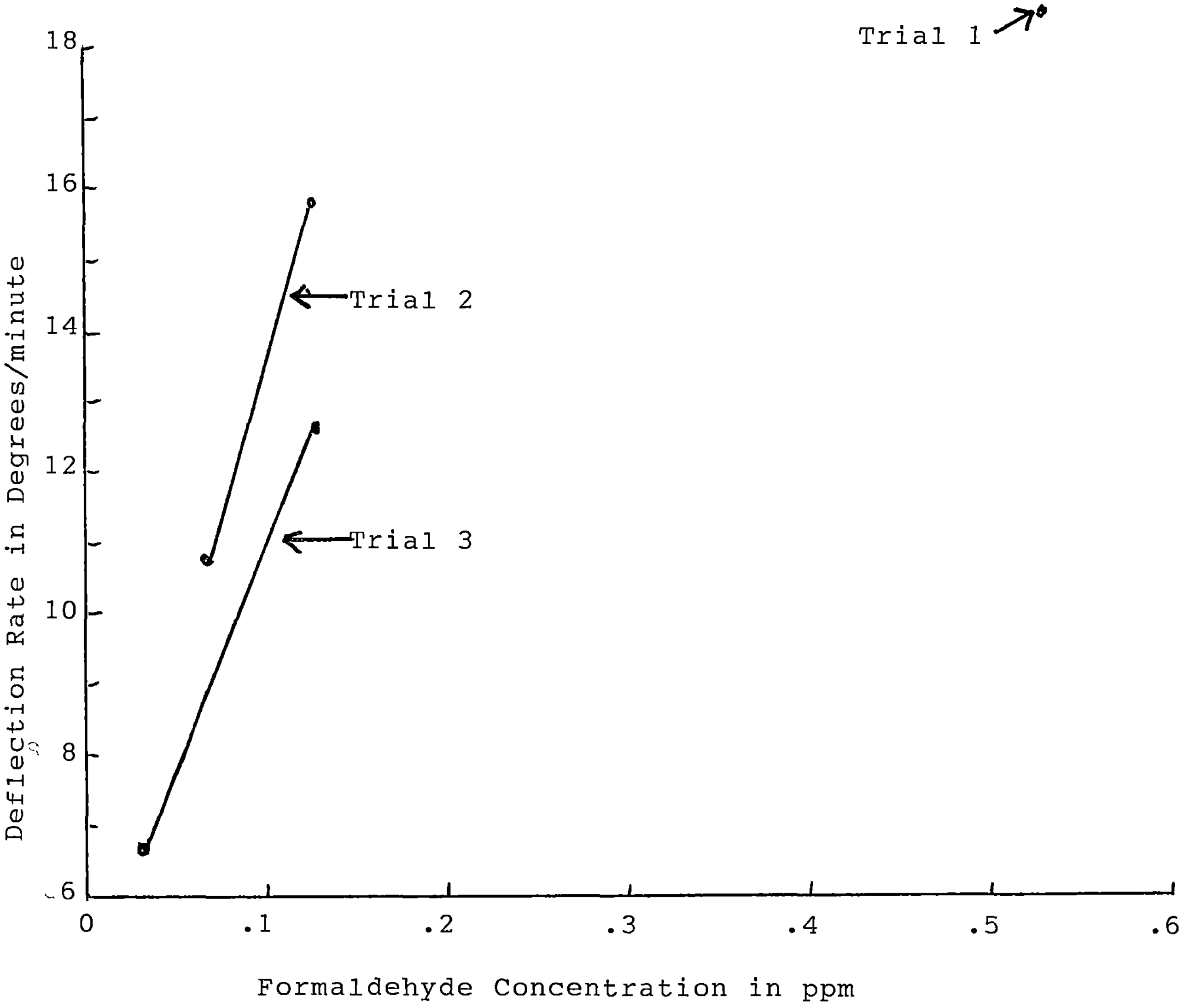


FIGURE 19 Formaldehyde Concentration vs. Deflection Rate



Over the course of experimentation both the drierite and molecular sieves were changed frequently.

A measured sample of acetone was obtained by means of a medical syringe (maximum of 0.5 ml) and inserted through a septum into a sealed 125 ml bottle. Once vaporized, a portion of the sample was obtained with a second syringe and inserted through a septum into the large 75 litre tank.

Although the same method was attempted for formaldehyde, the sample did not vaporize completely, and a second technique was developed. A sample was obtained using a medical syringe (maximum 0.5 ml) and placed on a Whatman filter. The filter was sectioned, and individual sections were suspended by means of a sample holder inside the 75 litre sampling tank.

4.2 RESULTS

The following sections describe the work done to characterize the performance of the VUV prototype as a detector for formaldehyde and VOCs, and the work done to establish the optimum operating conditions.

4.2.1 Factors which Affect Performance

The performance of the electroscope (linearity, gamma sensitivity), the effect of the corona atmosphere and argon flow rates on source characteristics, the influence of the air sampled on background, and the response of the prototype detector to samples of formaldehyde and acetone were studied.

i) Linearity

The rate of deflection of the electroscope leaf (discharge rate) while exposed to an alpha particle source was monitored over time (VUV source disconnected) to establish linearity. Some modifications to the leaf and field shaping shims were made to make the response more linear.

These results are presented in figure 16. The electroscope discharge curve is near linear and acceptable for the purposes of this research project. Linearity is influenced by many factors including dial accuracy, reading error, alignment of the dial to the electroscope leaf and the shape of the area around the leaf.

The effect of any non linearities on the measured deflection times was minimized by recording the time taken to deflect between two fixed angular positions.

ii) Deflection rate due to gamma background

Gamma radiation generates charge in the electroscope sensitive volume at a small and approximately constant rate. The charge so generated and any leakage current from the center electrode, slowly discharge the electroscope and act as a background. The purpose of this section was to establish the background deflection rate due to ambient gamma radiation and leakage currents.

With the alpha particle and VUV sources removed, the rate of deflection of the leaf was monitored by charging the electroscope to a deflection of about 50 degrees, then monitoring the rate of discharge for several weeks. The average deflection rate obtained for the electroscope was 2.4 degrees per day. This discharge rate is about ten times higher than expected for gamma background and corresponds to the amount of charge generated in a one liter volume (the volume of the electroscope is about 100 milliliters). The higher than expected rate of discharge, which is probably due to electrical leakage, is still acceptable for the purposes of this research since full scale deflection times are tens of degrees per minute with the VUV source turned on.

iii) Argon vs air as corona discharge gas

The nature of the gas atmosphere (argon vs purified air) in the source, gas flow rates, flow conditions (static or flowing) and the corona on/off status all influence the character of the corona discharge. Various experiments were done to establish the influence of each of the factors on the VUV output of the corona and subsequently the electroscope discharge rate. Thus the effect of static room air, static argon gas, and various argon and air flow rates were studied and some of these results are summarized below.

a) The ratio of discharge times corona on (Air,no flow) to no corona (Air ,no flow) was 658:1.
b) The ratio of discharge times Argon (flow of 1/6 L/min, corona) to Air (no flow, corona) was 8.7:1.
c) The ratio of discharge times Argon (flow of 1/6 l/minute, corona) to Air (flow of 1/2 l/minute, corona) was 108.

The air flow through the electroscope chamber was recirculated and the argon flow rate through the corona chamber adjusted to determine the optimum flow to be employed in most experiments. These results are presented in figure 17. An argon flow rate of 1/6 L/minute was used in all subsequent experiments.

iv) The influence of indoor, outdoor, and recirculated air flowing through the electroscope on the electroscope discharge rate.

Alternatively, recirculated air, inside air, and outside air were intercompared to determine the lowest background discharge rate possible. Various configurations for the pump, drierite and síeve traps were tried (recirculating air supply, vented air supply).

At a 0.5 L/minute airflow, the discharge rates (degrees/min) were;

a) Recirculating air	7.6
b) Inside air	51.5
c) Outside air	8.8

For both inside and outside air studies, the drierite was quickly exhausted. With recirculated air the system could be run indefinitely. In addition, the background decreased in proportion to the time that the air was recirculated. The values quoted are the lowest observed after the drierite had been changed and the system run for three days. The volume of the recirculating system for these measurements was initially 1/3 liter. When the 75 litre sample tank was incorporated, higher defection rates were noted.

4.2.2 Response to Formaldehyde And Acetone Samples

In the following studies the sensitivity of the prototype to formaldehyde and acetone samples was determined.

The samples were obtained by means previously described, and the samples were recirculated through the 75 litre sample chamber, the electroscope, drying column and molecular sieve column. Sample concentrations ranging from 0.03 parts per million to 0.533 parts per million were studied. The electroscope discharge rate as a function of time was employed as a measure of the response of the electroscope to these samples.

i) Acetone Concentration vs. deflection rate

	Trial 1		**Trial 2**	
Acetone in ppm	**Rate degrees /min**	**Difference Rdg-Bgnd**	**Rate Degrees /min**	**Difference Rdg-Bgnd**
Background	11.4	----	12.2	----
0.064			32.9	20.7
0.080	28.7	17.3		
0.128			44.7	32.5
0.160	38.5	27.1		
0.192			53.3	41.1
0.240	39.0	27.6		

All background measurements were taken just prior to the injection of a sample and after the air had been recirculated for at least one day. In addition, the background measurements were made after the Argon gas flow (1/6 liter /minute) and corona discharge had been on for at least 2.5 hours and the electroscope had been charged and discharged several times to improve performance (see platinum wire prototype detector).

The response to the injected sample was immediate (within 3-5 minutes after injection) and the results as presented are the average of 3 to 5 measurements.

The two sets of data were done approximately one month apart with various other testing done in between. The sieves were replaced once and the drierite chamber was first increased in size with fresh drierite added and, then the drierite replaced a second time.

The results for trial one and trial two both demonstrate that a significant response is observed for concentrations as low as 0.064 ppm. No time was available to establish the minimum detectable level (MDL). Improved sensitivity should be achievable with increased power to the source, a larger optical window, purer argon, or a larger sample size. With some effort, levels around 0.01 ppm should be detectable without increased complexity or cost.

The response to acetone increases in magnitude in a linear manner with increased concentration and, results are roughly comparable between the two trials.

In one of the trials, there does not appear to be any increased response with increased acetone concentration (0.16 ppm, 0.24 ppm) and a saturation effect or a sampling error may be responsible. Since the detector seems to respond in a reasonably linear manner up to 0.2 ppm, a sampling error is the most probable cause of the unexpected result.

ii) Formaldehyde concentration vs. deflection rate

Formaldehyde in ppm	**Rate Degrees /min**					**Difference Rdg-Bgnd**
Background	11.9	15.7	12.3	21.1	22.0	----
0.033	18.5					6.6
0.067		26.5				10.8
0.133			24.9			12.6
0.133				36.9		15.8
0.533					40.0	18.0

All background measurements were taken just prior to introducing the sample and after the air had been recirculated for at least one day. In addition, the background was measured after the Argon gas flow and corona discharge had been on for at least 2.5 hours and, the electroscope had been charged and discharged several times.

The response was slow and required about an hour to reach a peak discharge rate in the electroscope. The discharge rate was continuously monitored from the time the sample was injected until well after the discharge rate peaked (0.5 hour), in order to establish the performance characteristics of the formaldehyde sample. As with the platinum wire prototype the formaldehyde samples exhibited a different timing pattern to the acetone samples and this characteristic may provide clues to making the detectors more selective to individual VOCs.

The reported results are the average of 3 to 5 measurements and the samples were measured over a one month period. The formaldehyde sample was injected immediately following unsuccessful attempts to introduce samples via the same method as for Acetone (Trial 1). The drierite was changed just before Trials 2 and 3.

The detector shows an appreciable response to formaldehyde at concentrations as low as 0.03 ppm. This measurement is a very conservative estimate since the sampling method does not ensure that all of the formaldehyde has vaporized from the filter, and the calculated concentrations are probably much higher than the actual. Time was not available to confirm the actual formaldehyde concentration.

The response to formaldehyde increases with increasing concentration and, parallel runs appear to agree reasonably well. The results are qualitative at the present time and additional work is needed to improve the sampling procedure. The response to formaldehyde appears to be half that for acetone for most measurements and, the theoretical mechanism for this has not been investigated.

The fact that the detector responds to both acetone and formaldehyde indicates that it is non specific in nature. It is, however, useful as a TVOC detector for survey work and for establishing the presence of VOCs at very low levels. No other spot measurement methods for TVOC, with comparable sensitivity, are commercially available.

With additional work the specificity of the detector could be improved.

4.2.3 General Observations

i) Background variations

Background varied over the course of the experiments. Factors that influence the backgound are the drierite freshness, drierite column size and location, sieve freshness, sieve column size and location, sample chamber volume, and recirculating pump flow rate and it was difficult to control all factors. Further study may suggest ways of reducing the influence of these factors.

ii) Saturation

The system tends to saturate when the background is high or when high sample concentrations are measured. The range of measurement can be extended by increasing the VUV light output or altering the geometry of the VUV lamp.

iii) Speed of Response

At the present time, the response and cleanout times are long and, following a measurement, the system must be purged overnight before a sample can be measured. The corona and argon gas must be turned on for at least 2.5 hours prior to introducing a new sample, and after injection of the sample, there is an 0.5 hour delay before a maximum discharge rate is reached. Some or all of these delays might be eliminated or reduced with further study. Simply heating the system would improve response and cleanout times.

iv) Portability

The need for an Argon gas supply limits portability. Portability might be improved by filtering and recirculating the Argon gas, changing the pressure at which the corona occurs, or by developing a sealed lamp.

v) VUV Source

Alternate (corona) discharge sources might lead to more portable, lower power or faster responding VUV light sources. The VUV source reaches a constant emission rate slowly and the VUV output from the lamp is very sensitive to changes in the argon flow rate, and the purity of the gas employed. The source is complex, difficult to control, and there is a need for further study.

vi) Reproducibility

More data is needed to establish measurement reproducibility. Since the background varied over the measurement period, and the system responded slowly and in an unpredictable manner, it was difficult to obtain reliable data over a lengthy measurement period. An improvement in any of these parameters would make it easier to establish measurement reproducibility.

4.2.4 Conclusions

- The response to an applied radiation source is near linear for the design employed.
- The deflection rate due to leakage currents and background radiation is insignificant when compared to the deflection rates due to VOCs. Background due to incomplete purging of injected organic materials or trace level substances in the ambient air can easily reach deflection times comparable to injected samples at or around 0.03 parts per million or less.
- The argon based corona discharge VUV source has a significant affect on the electroscope discharge rate.
- The corona atmosphere (argon vs air, flow/no flow) significantly affects the quality of the discharge, discharge rates and/or VUV source intensity.
- The discharge rate of the electroscope is significantly affected by the argon flow rate.
- The discharge rate of the electroscope is affected by the origin of the air in the electroscope and by the airflow pattern; recirculated air, outside air and inside air cause increasingly larger background deflection rates respectively.
- The lowest background and longest term operation was obtained with a recirculating air supply operating at about 0.5 liters per minute.
- The discharge rate increases in a linear manner with increased concentration of acetone in the range from 0.064 to 0.240 ppm.
- The discharge rate increases with increased concentration of Formaldehyde in the range from 0.033 to 0.533 ppm.
- Although no time was available to establish the minimum detectable levels for formaldehyde and acetone and to optimize the performance of the detectors, the sensitivity achieved with the unoptimized prototypes is still acceptable for indoor air quality measurements.
- For the VUV detector the response to acetone is roughly twice that for formaldehyde and no mechanism for this difference was formulated.

- Since the detector responds to both formaldehyde and acetone it is non specific in nature and is best termed a VOC or TVOC detector.
- The response of the VUV and platinum wire prototypes to formaldehyde and acetone followed different timing patterns. Timing patterns may provide a simple means for making the detectors more selective to formaldehyde.

5.0 COMPARISON OF PERFORMANCE CHARACTERISTICS BETWEEN THE DETECTOR AND OTHER TRADITIONAL METHODS OF DETECTING AND MEASURING FORMALDEHYDE AND VOCS IN CANADIAN HOMES

A review and discussion of traditional methods of analysis are presented in the appendices.

The Canadian exposure guidelines for formaldehyde are 0.1 ppm ASTER and 0.05 ALTER. The WHO identified <0.05 ppm as a consensus level of limited or no concern.

The Platinum wire and VUV based prototypes both readily achieve minimum detectable levels that are below 0.05 ppm and, thus have acceptable sensitivity for measuring indoor air formaldehyde levels. The detectors are not formaldehyde specific and also respond to acetone which is a typical VOC. The platinum wire based detector responds to formaldehyde in a linear manner from 0.01 to 2.5 ppm, while the VUV based detector responds in a linear manner to acetone between 0.06 and 0.25 ppm. The response of the later detector to formaldehyde increases with increasing concentration in the range from 0.03 to 0.5 ppm, but the response may not be linear.

The only commercial instrument with this sensitivity is the CEA Model TGM-555-FD, which is a complex automated wet chemical method. The TGM-555-FD is not a survey instrument intended for continuous measurement, but is selective in response, and is an ASTM method. This instrument requires a trained operator and a lot of attention to operate.

Several relatively-expensive, PID-based continuous instruments are commercially available. These portable detectors are quick responding and intended for survey work but are expensive and not sensitive enough for indoor air measurements. They are sometimes used to locate sources or identify areas where levels are higher than 0.1 ppm. These instruments are not specific for formaldehyde, have limited lifetimes and the expensive PID tube requires frequent replacement.

Other methods for formaldehyde are based on active or passive dosimeters and usually require from 1 hour to a week for a measurement. An analysis step is required and this may mean shipping the sample to a laboratory. The detectors are specific for formaldehyde, sensitive, provide time-weighted-averages rather than instantaneous measurements and are less expensive than the commercial instruments mentioned above.

Commercial instruments which employ Infra-red, and Photo-acoustic detectors are not sensitive enough for measuring VOCs and formaldehyde at indoor air levels.

Other methods of detection for VOCs are generally based on passive or active sorption onto a sorbent, followed by analysis with a Gas Chromatograph. These methods require several hours to collect the sample, and a laboratory for analysis. They provide an average concentration for the sampling period. If a FID detector is employed in the GC then a measure of the TVOC is obtained.

Direct reading electronic detectors are sensitive to VOCs to about the 0.1 ppm. These instruments are useful as survey tools and are often employed to locate sources. There are no low cost detectors capable of directly reading VOC levels below 0.1 ppm.

The prototypes developed in this research are able to detect VOCs and formaldehyde to levels as low as 0.01 ppm (0.3 ppm tested for VUV based prototype), are low cost in nature, and relatively simple to operate and maintain. They should be more affordable by the home inspector and the homeowner than existing commercial instruments.

6.0 COMMENTARY ON THE APPROPRIATENESS OF THE TESTING TO DETERMINE THE STRENGTHS, WEAKNESSES AND LIMITATIONS OF THE DETECTOR INCLUDING ACCURACY, CALIBRATION REQUIREMENTS, MAINTENANCE AND OPERATIONAL EFFICIENCY ISSUES

The testing carried out in this research should be considered exploratory and serves to roughly outline the performance of the Platinum catalyst and VUV based detectors.

- Since the response to VOCs and formaldehyde are roughly the same, the methods are non specific. Time was not available to make the detectors more selective, but a number of promising strategies are being studied. The detectors at the present time can be classified as TVOC detectors.

- The calibration methods are based upon the injection of pure acetone and a 40% formaldehyde solution into a container of known volume. The concentrations were not confirmed by a second procedure or compared against reference methods. An accuracy of about +/-15 % was estimated for the procedures.

- The platinum-catalyst-based detector was sensitive to 0.01 ppm formaldehyde, while the VUV based detector gave a measurable response at 0.03 ppm for an unoptimized system. Although this level of sensitivity is adequate for indoor air work, lower levels would be readily detectable with small improvements in procedure and detector design.

- The platinum based detector responded in a linear manner in the range from 0.01 to 2.5 ppm. The VUV-based method was non linear but both methods did respond to Formaldehyde and VOCs at low levels.

- Limited information was obtained on stability and ruggedness. Over the 4 month test period ion currents and discharge times stayed relatively constant, and the heated platinum filament did not deteriorate. The filaments may eventually generate noise and become fragile at elevated temperatures but this was not investigated.

- The platinum catalyst detector was not sensitive to variations in ambient temperature and humidity at the operating temperature of around 800 C. Variations in the catalyst temperature however, affected the sensitivity of the detector.

- Some problems were experienced with background after injection of the formaldehyde sample, particularly when plastics were present in the sampling train. An attempt was made to construct the prototype of non absorbing materials but more work is required (heated detector). The speed of response of the detector is important since one of the objectives is to develop a portable survey instrument.

- Only limited work was done on reducing the power consumption of the platinum catalyst detector and/or making it more portable (reducing wire diameter, increasing length of wire, varying the wire geometry). The detector, as constructed, appeared to function adequately, and no time was available to further investigate these proposed improvements.
- No attempt was made to construct a static VUV source (no argon flow). Time was available to evaluate aspects of the flow through source (the later is probably too large or complex for a portable detector and a bottle of argon gas is required). The experiments illustrated the feasibility of detecting formaldehyde and VOCs by means of a VUV source.
- The research period was too short to establish the stability and lifetime of the VUV source. The window and source construction materials may deteriorate under prolonged exposure to VUV radiation.
- The VUV source characteristics were not extensively tested (applied power, size, reflectance of materials, window transmission and optimization, frequency range, geometry and discharge characteristics, argon airflow). The source was employed as designed and no attempt was made to improve the sensitivity or stability of the device.
- There is a need to evaluate the ability of the prototypes to measure other VOCs and mixtures of VOCs.

7.0 CONCLUSIONS REACHED AS A RESULT OF THE PROJECT INCLUDING ALL SUCCESSES AND/OR FAILURES

- The test program effectively demonstrated the ability of both technologies, in conjunction with an electroscope, to detect VOCs and formaldehyde at very low concentrations.

- The methods are non-selective at this stage and more work is required if a formaldehyde-specific or VOC-specific detector is the objective.

- The detectors are not ruggedized, or portable, nor is the performance optimized. More research is needed to characterize the detectors, to make them portable and to optimize their performance; some specific objectives being to reduce the power consumption and eliminate the argon tank.

- The work has indicated that low cost detectors are feasible and simple to construct. There is also the possibility of developing a direct reading low cost continuous detector which would employ an electrometer rather than an electroscope. The later could be developed as an instant survey meter or provide continuous measurement if connected to a logging device.

- A review of the literature has been made and summarized. Based on this review, some opportunities to develop formaldehyde detectors have been identified. The Platinum catalyst based technology was selected as one of the more promising methods.

8.0 APPENDIX A: RATIONAL FOR THE DESIGN OF PROTOTYPE DETECTORS

Two technologies which generate ions in the presence of formaldehyde and VOCs, and which may be combined with a simple electroscope ion measuring device, have been identified.

The methodologies (source) were chosen based on the following criteria. They should: generate an ion current in proportion to the level of VOC present; be safe; be relatively inexpensive; be reliable; be stable; be effective; and only generate currents in the presence of a VOC.

Corona and microwave VUV Photoionization sources, Corona and microwave discharge, Atmospheric pressure ionization, thermal (FID, heated platinum wire), radiation (X-ray, alpha particles, Beta particles, Tritium), and laser induced phtotoionization were all evaluated.

- Radiation sources are hazardous and are technically unsuitable because they constantly generate ion currents even in the absence of a VOC sample.

  As a result, the electroscope would constantly discharge, and the constant background signal would dominate the VOC signal, even at high concentrations.

  Attenuated Beta particles from tritium may not have enough energy to ionize air molecules, but may still effectively ionize VOCs (maximum energy about 18Kev). Although beta sources may offer promise as simple ion sources, it was decided to avoid radiation sources altogether.

- Corona and microwave based VUV photoionization sources are somewhat complex. A number of commercial instruments are available (HNU; Photovac) but both suffer from slow window deterioration and limited sensitivity (0.1 ppm MDL). Due to budget constraints, and the fact that Instruscience Ltd. has experience with corona discharge sources, research was limited to this type of system.

  The HNU and Photovac systems are not sensitive to VOCs at typical indoor air concentrations. The LLD of measurement may be improved by employing a very sensitive electroscope.

  The sources do not ionize air molecules and therefore do not generate a background ion current.

  Unless an inexpensive window material can be found, it is doubtful whether an inexpensive VUV source can be developed. LiF and CaF2 are relatively expensive to purchase in small quantities.

- Corona and microwave ion sources are continuous generators which will quickly discharge the electroscope detector (as do radiation sources) unless a methodology is developed to selectively monitor the ion fragments due to the VOC (ion mobility spectroscopy/mass spectroscopy). This research was considered to be beyond the scope and budget of the project.

- The heated platinum catalyst source, is simple in principle and may satisfy all project objectives, but little is known about this type of source. In several instances, it has been employed in conjunction with amperometric sensors.

- The FID detector was too complex for this project.

- Laser-induced photoionization has been employed as an effective method but the costs and complexity of setup prohibit study in this research.

9.0 APPENDIX B: LITERATURE REVIEW: FORMALDEHYDE DETECTION METHODS

9.1 Conclusions Reached in Terms of HTIP Project ;

- A catalytic reactor (platinum) offers promise as a low cost method for use with an electroscope or electrometer.

- Although only a corona-based VUV source will be evaluated in this research, the microwave reactor is also a promising technology and sources are commercially available.

- It may be feasible to adapt passive formaldehyde detectors for field readout by modifying the design to include a conducting substrate. As the formaldehyde is sorbed, the substrate conductance should vary and be easily measurable with a standard conductance meter.

- It may be feasible to extend the range of simple colorimetric tubes to indoor air levels by coupling them to a passive sampler and simple thermal desorber.

- There are no simple direct-reading electronic instruments suitable for formaldehyde measurement in indoor air. During informal conversation with several experts in the field a method based on infrared was identified (not part of this research) This approach is not commercially available.

- There appears to be a real concern over the usefulness and accuracy of many existing and accepted methods of measurement because of poor manufacturer and/or user quality control and limited sensitivity of the instrument.

- There are a number of promising new microsensors (chemical/biochemical) for selective formaldehyde measurement.

9.2 Detailed Summary of the Current State of the Art: Methods for Detecting and Ionizing Formaldehyde

The following section summarizes and interprets the information presented in the **Annotated Bibliography**

Methods of detecting and/or analysing for formaldehyde could include: direct reading spectroscopic (infrared, ultraviolet); ionizing or catalysis methods (thermal or flame, photo, radiation, corona or Penning discharge, Atmospheric Pressure Chemical Ionization); chemical (colorimetric, polarographic, HPLC, GC&GC/MS); electrochemical; microsensors; (chemical, biochemical); and/or photoacoustic.

i) Spectroscopic

There are no commercial spectroscopic analyzers with sufficient sensitivity to detect formaldehyde at typical indoor air levels. The Miran 1B infrared detector by Foxboro, a well established VOC detector, marginally achieves the target sensitivities. The cost of the unit is prohibitive at >$20,000. Some difficulty would be experienced with infrared detection methods since water absorption bands may interfere, and air scrubbers may also remove formaldehyde and/or build up an interfering background.

ii) Ionizing/catalysis methods

Ionization/catalysis methods either remove one or more electrons or decompose the molecule into ion fragments and neutral molecules. A corresponding current, due to the charged molecule or fragment (amperometric). Patterns (mass spectroscopy, ion mobility spectroscopy), or new neutral molecules (electrochemical or fuel cells), may be detected.

Thermal/catalytic;

Several sensors based on heated platinum filaments coupled to chemical sensors or electrometers were identified. No commercial instruments for formaldehyde based on this principle have been identified. This approach may be simple and very low cost.

Flame Ionization Detectors (FID) are suitable for chromatographs but are probably too sophisticated and expensive for low cost portable instruments.

Photoionization

Formaldehyde requires about 10.8 ev to ionize and this energy level is achieved in the vacuum ultraviolet (VUV), or by multiphoton laser methods.

VUV radiation is generated by microwave and corona gas discharge sources or by arcs. These technologies were reviewed and the corona/arc method selected for further study. It is the easier methodology to implement and still tests the feasibility of the concept proposed in this research project.

The microwave method may offer more flexibility in design, better stability and higher efficiency over the corona discharge method. Several electronic instruments based on microwave methods have been developed. The Photovac TIP instrument does not generate radiation with enough energy to ionize formaldehyde. The HNU instrument does, but the lamp employed has a short lifetime (3-4 months). Neither instrument is sensitive below 0.1 ppm however, and they will not detect formaldehyde at levels typically found in indoor air.

VUV generating lamps have limited lifetimes (months) due to window deterioration.

A method of laser-induced photoionization and analysis by fluorescence has been identified. Concentrations of formaldehyde down to 0.02 ppm were measured. No portable commercial instruments which employ laser technology have been developed. Although a promising strategy to employ for formaldehyde, the technology was considered to be too expensive and sophisticated for the proposed project.

Radiation ion sources

X-ray, and/or alpha/beta radiation are often employed as ionizing sources in instrumentation (electron capture detectors, ion mobility spectrometers, mass spectrometers).

These sources generate a constant current, however, which would quickly discharge the electroscope, unless a methodology is employed to selectively allow the formaldehyde ion fragments to transit to the collector electrode. This research was beyond the scope of this project.

Corona or Penning discharge ion sources

Corona discharge sources are being employed in this research as VUV generators. Both Corona and Penning type discharge sources are, like radiation sources, constant ion generators and are therefore unsuitable for direct use.

Atmospheric pressure chemical ionization mass spectrometry

This technology employs a corona discharge and a mass spectrometer. The SCIEX TAGA system will detect formaldehyde at indoor air levels (trace levels) but the system is expensive.

iii) Chemical Methods

Colorimetric

These methods collect formaldehyde either actively or passively, and after the addition of a colour forming chemical are analyzed spectrophotometrically (colorimetrically).

Active methods of collection employ impingers, a suitable solution (MBTH, Pararosanaline or Chromotropic acid), and a small pump. Sample times range from 1 to 8 hours and all methods are suitable for indoor air analysis. Extreme care must be taken to clean equipment since trace contaminants are a frequent cause of error.

Quality control is a major concern with formaldehyde measurement methods, particularly impinger methods. The impinger method enables the operator to take a quantitative measurement relatively quickly and the equipment is readily available.

Active colorimetric sampling tubes are available. The minimum detectable level is about 0.5 ppm even after many pump strokes and this method is not recommended for indoor work.

A method of analysis which includes a combination of passive sampling, thermal desorption and short term colorimetric tubes has been identified. This approach, if simplified, may offer a useful strategy for extending the range of colorimetric tubes to indoor air analysis.

Passive methods are available based on the MBTH, and Chromotropic acid methods. These methods require 8 hours to 7 days for a measurement and all have a claimed sensitivity of 0.01 ppm or less. The MBTH method is an ASTM technique. In all cases, triplicate samples, outdoor references and strict attention to quality control by the manufacturer and user are very important considerations.

A continuous instrument based on the pararosaniline method is available for indoor air measurements (EPA and ASTM standard). This is an expensive and complicated monitor designed for continuous measurement. A trained operator is required.

iv) Polarographic

A polarographic method is available with a quoted minimum detectable level of about 4.8 ppm. The dropping mercury electrode is a laboratory method which may eventually be adapted to indoor air measurements.

v) HPLC

This method involves the active or passive collection of formaldehyde on a DHPH impregnated substrate, followed by elution with acetonitrile, and analysis by HPLC.

It has been employed by several groups including the USEPA where it is being recommended as a reference method.

The advantage is that a sample can be collected relatively quickly and accurately at indoor air levels.

vi) GC/GC/MS

An air sample can be analyzed by GC or GC/MS, either by direct injection of an eluted liquid sample, or by thermal desorption of the sample, followed by analysis with an appropriate detector (PID, FID, MS).

Several portable gas chromatographs have been identified (Photovac, Sentex, Thermo Electron, and Cavendish Labs). These instruments are too complex and expensive.

vii) Electrochemical

A direct reading electronic instrument based on fuel cell technology has been identified. This detector is not sensitive at indoor air levels.

viii) Microsensors

Enzyme and chemical based piezoelectric sensors are being developed. These devices offer promise as low cost devices for continuous formaldehyde measurement, but are not commercially available at the present time.

The sensors are constructed of a piezoelectric crystal coated with a selective chemical or enzyme. The crystal changes frequency in proportion to the VOC (formaldehyde) concentration.

This approach to formaldehyde detection was considered to be too long term and risky to be included in the present research project.

ix) Photoacoustic Methods

One instrument has been identified (Bruel and Bjaer). It will simultaneously measure a number of air quality parameters (CO2, CO, VOCs, Humidity, Temperature) but it is not sensitive enough to measure formaldehyde at indoor air levels. The instrument has a claimed minimum detectable level of 0.5 ppm. The technology is very sophisticated and beyond the scope of this project.

10.0 APPENDIX C: ANNOTATED BIBLIOGRAPHY: FORMALDEHYDE METHODS OF MEASUREMENT

In this bibliography methods for ionizing molecules and the state of the art in formaldehyde detection are reviewed. The review formed the basis for the final design of several prototype formaldehyde detectors (HTIP project).

The study focused on identifying methods for ionizing organic molecules which can be employed with an electroscope, are low cost, sensitive at residential indoor levels, insensitive to interferences, portable and safe.

The first section of the bibliography, 10.1, presents methods for ionizing formaldehyde (ionization potential 10.8 electron volts).

The second section, 10.2, presents methods of detection.

10.1 Part One; Methods for Ionizing Formaldehyde and Background Information

Keyword Methods;

- **Photoionization**
  - **Laser**
  - **Vacuum Ultraviolet sources (Corona/arc/microwave discharge)**
- **Corona (DC/AC) Discharge**
- **Radio Frequency and Microwave discharge**
- **Flame Ionization**
- **Chemical Ionization**
- **Thermal (Pyrolysis/catalysis)**
- **Radiation (X-ray, Alpha particle, Beta particle)**

1. Portable Photoionizers, Product Bulletin of HNU Systems Inc., Newton, MA, (1993)

2. HANDBOOK OF CHEMISTRY AND PHYSICS, Wheast, R. C., Editor in Chief, The Chemical Rubber Co., Cleveland, Ohio, E-61, (1965)

3. Zaidel A. N. and Schreider E. Y., VACUUM ULTRAVIOLET SPECTROSCOPY, Ann Arbor-Humphrey Science Publishers, Ann Arbor, Michigan, (1970)

This text covers Radiant Energy Sources and Optical Materials used in VUV Spectroscopy to 1970. Of Particular interest are the Inert Gas Continua produced by these various sources. Argon appears the most suitable with continua from 1067A. Also Optical Material LiF is discussed.

4. Garber, C., A STUDY OF THE GENERATION OF VACUUM ULTRAVIOLET RADIATION FROM DISCHARGES IN HELIUM, University Microfilms

International, Ann Arbor Michigan, (1976)

An analysis and comparison of the helium emission from C.W. Microwave, Pulsed Microwave and Pulsed D.C. excitation were performed in order to determine the factors affecting emission intensity and spectra.

5. Sneddon J., and Bet-Pera F., "Electrothermal vaporization-inductively coupled plasma emission spectrometry", TRENDS IN ANALYTICAL CHEMISTRY, Elsevier Science Publishers, (1986)

The use of electrothermal vaporization for sample introduction to the inductively coupled plasma for emission spectrometric determination of elements in complex samples is discussed. The advantages and disadvantages, analytical performance characteristics, and ease of operation as compared to conventional pneumatic nebulization and other sample introduction techniques, are described.

6. Jaffe, H. H., and Orchin, M., THEORY AND APPLICATION OF ULTRAVIOLET SPECTROSCOPY, John Wiley & Sons, (1962)

This covers fluorescence Spectra-conditions for fluorescence, the wavelengths and vibrational structure of fluorescence spectra, decay periods and special effects in fluorescence.

7. Byram, E. T., Chubb T. A., and Friedman H., "Solar X-Ray Spectrum Analysis", JOURNAL OF GEOPHYSICAL RESEARCH, 61 ,251, (1956)

Mylar and Glyptal were studied as windows for X-Ray transmission

8. Schneider, E.G., "The Effect of Irradiation on the Transmission of Lithium Fluoride", JOURNAL OF THE OPTICAL SOCIETY OF AMERICA, 27, 72, (1937)

The transmission of lithium fluoride in the visible and ultraviolet may be considerably reduced by exposure to very intense ultraviolet radiation, electron bombardment or contact with a low pressure electrical discharge. Strong absorption bands with maxima at 5200,3100, and 2500A and a gradually increasing absorption below 1800A appear after a few minutes exposure to electron bombardment or contact with the low pressure discharge. Since 75 hours exposure to the light of a hydrogen discharge tube caused only about a maxima decrease of 5% in transmission, lithium fluoride may be considered as satisfactory as fluorite for use in ultraviolet optical instruments. Since all of the absorption bands build up at about the same rate, the visible discoloration, faint yellow to deep red, may be used as an indication of the change in the ultraviolet. Lithium fluoride coloured by irradiation may be useful as a filter in ultraviolet studies.

9. Patterson, D. A., and Vaughan, W. H., "Influence of Crystal Surface on the Optical Transmission of Lithium Fluoride in the Vacuum-Ultraviolet Spectrum", JOURNAL OF THE OPTICAL SOCIETY OF AMERICA, 53, 851, (1963)

A selective decrease in the spectral transmittance of cleaved LiF crystals at wavelengths shorter than 1600A has been observed when they are exposed to the atmosphere. The decrease is attributed to a surface layer produced on the crystals by reaction with moisture. It can be substantially inhibited by immediate post-cleavage storage in dry gas or in vacuum. Optical-quality thin plates of currently available, commercial hard-to-cleave LiF that is softer than LiF previously manufactured can be obtained by first hardening the crystal with X-rays, cleaving the plates, and then thermally annealing out the optical effects of the X-rays.

10. Warneck, P., "LiF Colour-center Formation and uv Transmission from Argon and Hydrogen Discharges", JOURNAL OF THE OPTICAL SOCIETY OF AMERICA, 55, 921, (1965)

The transmission losses of lithium fluoride used in conjunction with vacuum-ultraviolet sources were investigated and found to originate mainly from LiF colour-center formation caused by absorption of radiation in the LiF fundamental band. The observed absorption features have been studied, including bands at 1120, 2500, 4500 and 6200A in addition to a continuum in the 1000-3000A wavelength region. The continuum and the bands at 1120 and 2500A were found to be primary features, while the 4500 and 6200A bands are of secondary origin. The 2500A band was shown to be the lithium fluoride F band.

11. Hunter, W. R., Angel, D. W., and Tousey R., "Thin Films and Their Uses for the Extreme Ultraviolet", APPLIED OPTICS, 4, 891, (1985)

The transmittance characteristics in the extreme ultraviolet of unbacked films are discussed; data are presented for films of Al, In, Bi, Ge, Si, and certain organic materials. Generally, the metals begin to transmit shortward of their critical wavelengths, determined by the electron eigenloss, and reach maximum transparency at the nearest X-ray edge; to shorter wavelengths regions of transparency exist between the other X-ray edges. Their use in order-sorting, and for eliminating long-wavelength stray light, is illustrated with laboratory spectra and solar spectra obtained from rockets.

12. Messman, J. D., O'Haver, T. C., and Epstein, M. S., "Evaluation of a Direct-Current Argon Plasma as a Primary Pseudocontinuum Radiation Source for Wavelength-Modulated Atomic Absorption Spectrometry", ANALYTICAL CHEMISTRY, 57, 416, (1985)

A direct-current argon plasma (DCP) pseudocontinuum source is investigated as an alternative to a Cermax xenon arc continuum lamp (XAL) for wavelength-modulated continuum-source atomic absorption spectrometry (WM-AAC), particularly for the determination of elements in the lower ultraviolet wavelength region. The emission line from the DCP source is intentionally broadened by aspirating a large concentration of analyte solution into the plasma so that it appears as pseudocontinuum radiation over the narrow wavelength modulation interval. The DCP source significantly reduces both order overlap and far stray radiation compared to the XAL, but signal-to-noise ratios are degraded relative to the XAL source because of plasma-emission self-reversal flicker noise.

13. Xueji Xu, "A Slit Shaped Light Source for VUV Radiation", PROCEEDINGS OF THE 8TH INTERNATIONAL CONFERENCE ON GAS DISCHARGES & THEIR APPLICATIONS, Pergamon Press, (1985)

Reported here is a new type of rare gas radiation source, an a. c. source operated at pressures of one atmosphere or less, that has uniform radiance, is free of contaminant lines, is low power and is reproducible.

14. Marchetti, R., Penco, E., and Salvetti, G., "A New Type of Corona-discharge Photoionization Source for Gas Lasers", JOURNAL OF APPLIED PHYSICS, 56, 3163, (1984)

Presented are results of an experimental study aimed at characterizing a new type of corona-discharge photon source, which is particularly suitable to be used as preionizer in transversely excited gas lasers operating at high pulse repetition frequencies. Results of comparative tests carried out in CO2 laser gas mixtures between this photoionization source and a conventional bare spark source are also reported, showing the superiority of the proposed scheme.

15. Marchetti, R., Penco, E., Armandillo, A., and Salvetti, G., "Optimization of Corona-discharge Photoionization Sources for CO2 Lasers", JOURNAL OF APPLIED PHYSICS, 54, 5672, (1983)

The results of an experimental study of ultraviolet photoionization produced by a corona discharge in CO2 laser gases are reported. The influence of corona discharge physical and electrical parameters on the produced photoelectron density is investigated so that an optimized design of these types of photoionization sources can be achieved.

16. Fransson, J., and Jansson, E. V., "The STL-Ionophone: Transducer properties and construction", JOURNAL OF THE ACOUSTIC SOCIETY OF AMERICA, 58, 910, (1975)

The STL-ionophone is a simple electroacoustical transducer well suited to many applications in an acoustic laboratory, even one with modest equipment. Its transducer element consists of a glow discharge in the atmospheric air, which is initiated and maintained by a highly stable dc power supply and a large current limiting resistor. In this report how the correct discharge is obtained is presented along with basic transducer properties of the discharge.

17. McLuckey, S. A., Glish, G. L., Asano, K. G., and Grant, B. C., "Atmospheric Sampling Glow Discharge Ionization Source for the Determination of Trace Organic Compounds in Ambient Air", ANALYTICAL CHEMISTRY, 60, 2220, (1988)

A new atmospheric sampling ion source, based on the establishment of a glow discharge in ambient air drawn into a region of reduced pressure, is described. The source is simple, rugged, and relatively maintenance-free, exhibits a very short memory, and is extremely sensitive for compounds with high proton affinities, high electron affinities, high gas-phase acidities, and/or low ionization potentials. The effects of discharge voltage and source pressure on the nature of the mass spectra observed are described. These operating parameters affect the absolute number of ions observed and, particularly for positive ions, affect the distribution of the reagent ions and the degree of fragmentation. For illustrative purposes, the limit of detection and dynamic range of the ion source coupled with a mass spectrometer are discussed for 2,4,6-trinitrotoluene. For the present system, a detection limit of 1-2 parts per trillion and a linear dynamic range of at least 6 orders of magnitude are observed.

18. Binur, Y., Shuker, R., and Szoke, A., "Fast Electrical Discharge Tube for Time Dependent Spectroscopy", REVIEW OF SCIENTIFIC INSTRUMENTS, 46, 472, (1975)

An improved transverse discharge tube for time resolved spectroscopy is described. Current densities of 1000 A/cm2 with rise time of less than 5ns and total pulse length of 30 ns were achieved in pressures up to 500 Torr of noble gas mixtures. This improved performance, compared with the Tanaka longitudinal tube, is essential for observation of fast energy transfer processes originating at highly excited atomic and molecular levels.

19. Carlson, R. W., "A Fast Continuum Light Source for the Extreme Ultraviolet", REVIEW OF SCIENTIFIC INSTRUMENTS, 42, 171, (1971)

The purpose of this note is to describe an extreme ultraviolet continuum light source which has been found suitable for photoelectric techniques, in particular the measurement of absolute photoabsorption cross sections and the study of fluorescence resulting from the photographic absorption process.

20. Ausloos, P., and Lias, S. G., "Gas Phase Photolysis of

Hydrocarbons in the Photoionization Region", RADIATION RESEARCH REVIEW, 1, 75, (1968)

Light Sources including Resonance Lamps and Monochromators are discussed with some construction techniques and major resonance lines of various inert fill gases.

21. Haarsma, J. P. S., de Jong, G. J., and Agterdenbos, J., "The Preparation and Operation of Electrodeless Discharge Lamps-A Critical Review", SPECTROCHIMICA ACTA, 29B, 1, (1974)

In this paper the literature on electrodeless discharge lamps (EDLs) is reviewed. Several aspects of preparation and operation of EDLs are critically discussed. Attention is also paid to multi-element EDLs and comparisons of EDLs with other light sources. The authors feel that the present situation must be characterized by the conclusion that really concrete and general conclusions cannot be drawn from the literature.

22. Levy M. E., and Huffman, R. E., "Vacuum Ultraviolet Plasma Arc Radiation Source for the 300-1000 A Wavelength Region", APPLIED OPTICS, 9-1, 41, (1970)

A plasma arc radiation source is described which can produce continuum radiation in the 300-1000A range from discharges in the gases He, Ne, Ar, Kr, Xe, H2 and their mixtures. The radiation is emitted from a dc self-stabilized plasma arc column having a core temperature of about 18,000 K. The spectra of major interest are due to ion-electron recombination to the ground state of the neutral atom. These continua extend to wavelengths shorter than the first ionization threshold. For helium, the useful continuum extends from 504A to approximately 350A. The arc column is observed along its cylindrical axis of symmetry through a small opening in the anode. The radiation source was developed for use in the measurement of cross sections in the vacuum uv using continuously scanning photoelectric spectrometers. The application of the source to measurements in krypton near 500A is described.

23. Rustgi, O. P., "Transmittance of Thin Metallic Films in the Vacuum-Ultraviolet Region Below 1000A", JOURNAL OF THE OPTICAL SOCIETY OF AMERICA, 55-6, 630, (1965)

The transmittance of titanium, tellurium, antimony, beryllium, aluminum, gold and silver films has been measured in the vacuum-ultraviolet region below 1000A, using a 1-m Seya monochromator together with a line-emission capillary spark source. In Ti, transmittance started at 18eV, as observed earlier, rose to a peak value at 31.5eV, then decreased to less than 0.1% near 38eV, characterizing the M2,3 absorption edge. The transmittance in Te has been measured from near its threshold at about 15eV to a maximum at 38eV, followed by a sharp drop between 39 and 40eV and a subsequent rise towards shorter wavelengths. Antimony exhibited an onset of transmittance near 15eV, increasing to a maximum near 31eV, from where it rapidly decreased to zero at 33eV. At 37eV it rose again to a second maximum at 39.5eV and went to zero at 42eV. In Be, transmittance began near 19eV, which is compared to nearby values of both the plasma frequency and characteristic electron energy losses. Some new transmittance curves for Al, Extended towards shorter wavelengths than reported in earlier work, are also presented here, primarily because Al films were used as a backing layer for the measurements on Te, Sb, and Be films. No transmittance was observed in Ag and Au films down to 250A.

24. Goode, S. R., Baughman, K. W.,Pipes D. T., and Sandridge, M. R., "Fabrication and Utilization of a High-power Microwave Supply for Electrodeless Discharge Lamps and Other Spectrochemical Emission Sources", APPLIED SPECTROSCOPY, <u>35</u>-3, 308, (1981)

A study of the factors influencing the performance of a microwave-induced discharge shows that the analytical utility generally increases as the applied microwave power is increased. The fabrication of an easily used high-power system (500 W) is described; the system is used to excite electrodeless discharge lamps of relatively high-boiling species, multielement lamps, and an atmospheric-pressure flowing plasma. The system has been used to study vaporization phenomena in a cadmium electrodeless discharge lamp. The ground-state atom population, as measured by absorption, appears to be directly related to the thermal (wall) temperature.

25. Goode, S. R., and Baughman, K. W., "A Review of Instrumentation Used to Generate Microwave-Induced Plasmas", APPLIED SPECTROSCOPY, <u>38</u>-6, 755, (1984)

The development and the design of instrumentation used to generate a microwave-induced plasma (MIP) is reviewed. Microwave power generators, coupling devices, discharge tubes, and their influence on the spectrochemical utility of the MIP are described. A complete analysis of the widely used TM 010 cavity is also presented.

26. Meiners, L. G., and Alford, D. B., "Simple Low-cost Microwave Plasma Source", REVIEW OF SCIENTIFIC INSTRUMENTS, <u>57</u>-2, 164, (1986)

A generator-cavity system is described which is capable of delivering 0-600 W of microwave power at 2.45 Ghz. The power generating section has been constructed from components contained in a portable home microwave oven and the cavity was assembled from easily machinable pieces. The C.W. magnetron source was mounted directly on a cylindrical microwave cavity. The plasma was contained in an on-axis 20-mm o.d. quartz tube. Design tradeoffs and operating information are discussed.

27. Fehsenfeld, F. C., Evenson, K. M., and Broida, H. P., "Microwave Discharge Cavities Operating at 2450 Mhz", REVIEW OF SCIENTIFIC INSTRUMENTS, 36-1, 294, (1965)

Five simple microwave cavities for producing discharges in gases were tested in He and H2 at pressures from 1u to 1 atm. Three of the cavities are commonly used, and two have been recently designed. One of the newly designed cavities offered a considerable improvement over early models with respect to compactness, ease of attachment to the system, and efficiency.

28. McCaroll, B., "An Improved Microwave Cavity for 2450 Mhz", REVIEW OF SCIENTIFIC INSTRUMENTS, 41, 279, (1970)

Using a 2450 Mhz microwave source a modified Evanson cavity is introduced which permits adjustment of the reflected power to less than 1W.

29. Baim, M. A., Eatherton, R. L., and Hill H. H., "Ion Mobility Detector for Gas Chromatography with a Direct Photoionization Source", ANALYTICAL CHEMISTRY, 55, 1761, (1983)

An ion mobility detector (IMD) for gas chromatography has been modified to accept the use of a photoionization source. Photoionization offers a number of advantages over the commonly employed Ni 63 foil including the lack of reactant ions, which are seen with the secondary ionization source, enabling use of the entire ion mobility spectrum from 0 to 20 ms for observation of product ions..Test compounds continuously bled into the detector are used to compare performance of the standard Ni 63 foil to that of a low pressure 10.0 Ev Krypton photoionization lamp. Due to uncomplicated fragmentation patterns produced via photoionization, the tunable selective capabilities of the detector are enhanced. Selective mobility monitoring is used to detect toluene, methylene, and naphthalene in a mixture of aromatic compounds of similar structure following separation on a fused silica capillary column.

30. Davis, D., and Braun, W., "Intense Vacuum Ultraviolet Atomic Line Sources", APPLIED OPTICS, 7-10, 2071, (1968)

Intense atomic lines (O, N, S, C, Br, Cl, H, Se, Kr) have been produced by microwave excitation of mixtures of gases in helium under flow conditions. The intensities generally obtained are greater than 10exp14 quanta/sec and are suitable for atomic emission studies and as photochemical light sources in the vacuum uv. Conditions for producing these high purity line sources are discussed.

31. Kinsinger, J. A., Stebbings W. L., Valenzi, R. A., and

Taylor, J. T., "Spectral Evaluation of a Sealed Helium Discharge Lamp for Studies in Photoelectron Spectroscopy", ANALYTICAL CHEMISTRY, 44-4, 773, (1972)

The construction and spectral properties of a windowed helium microwave discharge lamp for application to studies in photoelectron spectroscopy are presented. The 584A light flux passing a 1500A thick aluminum window from a 10mm i.d. discharge is in excess of 10exp13 photons/sec. These intensities permit fluxes of 10exp11-exp12 photons/sec in a PES source and are sufficient to produce photoelectron spectra of high resolution without spectral interference from impurity lines. Operation of the lamp at lower pressures produced the He II line at 304A. The intensity of this line relative to the 584A line could be obtained routinely at 1-5% and intermittently up to 50%. Applications of filter techniques are discussed which might increase the 304A intensity in this type of discharge, or others employed for PES studies.

32. Klein, A. G., Caspar, M. J., and Nicola, A., "Simple alpha particle detector", AMERICAN JOURNAL OF PHYSICS, 53-2, 1212, (1985)

A simple spark counter consisting of a 4-mil wire and a conducting ground plane is described.

33. Eichholz, G. G.,"The Rosenblum Spark Counter", Nucleonics, 10-10, 46, (1952)

Two new designs for a wire spark counter make it possible to construct a cheap, rugged, low-background instrument for alpha counting. The counter operates at 3000-5000 volts, has marked directional properties, needs no amplifier, and is better than a scintillation counter in certain instances.

34. Bella, F., Franzinetti, C., "Spark Counters", IL NUOVO CIMENTO, 10-10, 1461, (1953)

An account is given of a series of experiments which have been undertaken in order to investigate the main characteristics of spark counters. Part I gives details of the construction and presents the experimental results. In Part II the experimental results are discussed.

35. Louboutin, R., "Parasitic Discharge Phenomena in Ozonizers Filled with Glass Dielectric Tubes, and their Elimination", OZONE: SCIENCE AND ENGINEERING, 6, 123, (1984)

The operating voltage of a conventional concentric-tube type ozonizer is usually limited by the appearance of a spark phenomenon. This results from the concentration of electrostatic charges caused by the point effect at the level where the inner

metal coating of the glass dielectric tube stops, this foil being connected to the alternating high voltage source.

A graphic study of the phenomenon permitted the development of a device designed to homogenize the electric field at this level; as shown by experiments, this device eliminates the phenomenon of parasitic discharges.

Thus, the ozonizers fitted with this device can operate safely under high voltages.

36. Peyrous, R., and Lacase, C., "Technological Parameters that Influence the Production of Ozone in a D.C. Corona Discharge", OZONE: SCIENCE AND ENGINEERING, 8, 107, (1986)

Experiments using dry oxygen in a wire-to-cylinder ozone generator, submitted to D. C. corona discharges show that technological parameters (diameter and composition of wire and cylinder, length of cell, gas flow and transit time of the gas) greatly influence ozone production. The cell geometry to be used depends on the polarity of the D. C. voltage applied to the wire and, for a predetermined design, the maximum ozone production rate will be obtained by seeking the most suitable gas flow. Lining up a series of optimized cells can give significant results.

37. Phillips, R., SOURCES AND APPLICATIONS OF ULTRAVIOLET RADIATION, Academic Press, (1983)

This text covers many aspects of Ultra-violet radiation including: Applications, Photochemistry, Radiometry, Incandescent sources, Gas Discharges, Mercury lamps, Electrodeless lamps, Xenon lamps, Lasers,Irradiators, and Hazards.

38. High Performance Detectors for Gas Chromatography, Product Bulletin from Tremetrics Inc, Austin, Texas, (1993)

39. An Innovative Photoionization Detector for Air Analysis, Product Bulletin from Photovac Inc., Huntington, New York, (1993)

40. Light Sources, Product Bulletin from Resonance Ltd. Alliston, Ontario, (1993)

41. Radiation Sources for Research Industry Environmental Applications, Product Bulletin from Isotopes Products Laboratory, Burbank, California, (1993)

42. Crystal Optics, Product Bulletin from Bicron, Solon, Ohio, (1993)

43. Inorganic Phosphors and Related Chemicals - A Reference - , Product bulletin from Sylvania, Towanada, Pennsylvania, (1990)

44. Knoll, G. F., RADIATION DETECTION AND MEASUREMENT, John Wiley & Sons, New York, (1979)

45. Stetter, J. R., Findlay, M. W.,MacLay, G. J.,Zhang, J., Vaihinger, S., and Gopel, W., "Sensor Array and Catalytic Filament for Chemical Analysis of Vapors and Mixtures", SENSORS AND ACTUATORS; B1, 43, (1990)

An amperometric sensor array has been interfaced to a catalytic microreactor. The apparatus has been automated so that frequency- and amplitude-modulated concentrations can be produced for subsequent detection by the sensor array. The response of the CO sensor to modulated concentrations of CO, benzene, TCE, formaldehyde and perchloroethylene has been studied at different frequencies. The results reveal the operating principles and suggest that a simplified modulator-sensor system may provide enough information to identify and quantify individual compounds in simple mixtures.

46. Sears, W. M., Moen, V. A., Miremadi, B. K.,Frindt, R. F., and Morrison, S. R., "Positive Ion Emission from a Platinum Hot Wire Gas Sensor", SENSORS AND ACTUATORS, 11, 209, (1987)

It was found that hot (500 C to 1000 C) metal wires in contact with organic vapors or contaminated by surface carbon will emit positive ions in air. With appropriate bias and collection geometry, currents up to 100nA can be detected. As the carbon burns on a contaminated wire and the wire becomes cleaner, the current decays to zero. A clean platinum wire that is a good oxidation catalyst produces a steady positive ionic current in the presence of organic vapors. A number of different vapors were tested and it was concluded that higher responses were obtained for vapors with higher numbers of carbon atoms per molecule and greater ease of oxidation by the wire. Oxidizable gases with little or no carbon produced little or no ionic response. The Saha-Langmuir equation is used to calculate the ionization energies required to emit positive ions from the surface of the hot metal wire. This gave ionization potentials of about 6 Ev, which are too low to represent ionization potentials for carbon itself or an oxide of carbon and therefore must represent some, as yet unknown, intermediate of the oxidation reaction. It is concluded that both the clean and carbon-contaminated wire responses can be used to design selective gas sensors. At 800 C, for example, a clean platinum wire works as a highly reproducible gas sensor, giving a linear response from about 10ppm to 1% vapor concentration of acetone.

47. Stetter, J.R., Zaromb, S., Findlay, M. W. Jr., "Monitoring of Electrochemically Inactive Compounds by Amperometric Gas Sensors", SENSORS AND ACTUATORS, 6, 269, (1984)

Gas samples were exposed to a heated platinum element or gold filament before being introduced into the sample chambers of different amperometric sensors of the three electrode type.

The responses of four different sensors were measured. Of the ten compounds tested only two elicited significant responses without the filament. With the filament heated to 700 C each of the tested compounds elicited a significant response. The responses were proportional to concentration in the 0-50 ppm range.

48. Unwin, J., Walsh, P.T., "Monitoring Organic Vapours Using Pyrolysis-Amperometry", SENSORS AND ACTUATORS, 17, 575, (1989)

A sensor for toxic organic vapours is described. It is based on the technique of pyrolysis-amperometry, which involves pyrolysis of the vapour by heated catalytic elements and detection of the products by amperometric electrochemical cells. Suitable choice of catalyst allows the pyrolyser to be operated at lower temperatures, resulting in longer lifetime and lower power consumption of the sensor. The device can be used to measure directly concentration in ambient air or as part of a personal monitoring system to determine exposure. Here the sensor measures the amount of vapour thermally desorbed from a diffusive sampler.

49. Vaihinger, S., Gopel, W., "Detection of Halogenated and Other Hydrocarbons in Air: Response Functions of Catalyst/Electrochemical Sensor Systems", SENSORS AND ACTUATORS, B4, 337, (1991)

A method is described for analysing gases and vapours with amperometric sensors connected to a catalytic microreactor. As a practical example the analysis of a gas mixture with the dour components, carbon monoxide, formaldehyde, benzene, and perchloroethylene is discusses, with particular emphasis on solving cross sensitivity problems.

10.2 Part Two; Methods of Formaldehyde Measurement and Related Background

Keyword Methods;

Microsensors (enzyme or chemical/piezoelectric)
Bioluminescence
Laser fluorescence
Fluorescence
Pyrolysis-amperometry (electrochemical)
Fuel cells
Polarography
Chemical
    Adduct
    MBTH
    DNPH
    Pararosaniline
    Chromotropic acid
    Passive dosimeters

(Note the formaldehyde conversion factors ; 120 ug/m3 = 0.1 ppm)

50. Katritzky, A. R., Lam, J. N., and Faid-Allah, H. M., "Synthesis of New Microsensor Coatings and their Response to Test Vapours", TALANTA, 38-5, 535, (1991)

Novel 1,3,5-triazine derivatives were spray-coated onto surface acoustic wave (SAW) devices and exposed to vapors of dimethyl methylphosphonate (DMMP), chloroethyl ethyl sulfide (CEES) and water. Changes in chemiresistor and SAW responses were monitored and recorded by computer-controlled data-acquisition techniques. All the derivatives tested showed little or no chemiresistor or SAW responses to water vapor. The largest reversible chemiresistor response to DMMP vapor was observed with the dicarboxylic acid derivative. The largest SAW response to DMMP was with the dithione, and the dichloro-octylthio derivative showed the largest response to CEES.

51. Ho, M. H., and Richards R. A., "Enzymatic Method for the Determination of Formaldehyde", ENV. SCI. and TECH., 24, 201, (1990)

This paper describes a sensitive method for the determination of formaldehyde using two sequential reactions catalysed by two enzymes, formaldehyde dehydrogenase and diaphorase. The principle of this method is based on the quantitative oxidation of formaldehyde, in the presence of formaldehyde dehydrogenase and oxidized nicotinamide adenine dinucleotide (NAD), to produce formic acid and the reduced dinucleotide (NADH). The NADH produced then reacts with oxidized 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyltetrazolium (INT), in the presence of diaphorase, to produce formazan, a highly chromogenic compound. The formazan formed is measured spectrophotometrically at 500nm and will be directly proportional to the amount of formaldehyde in the assay solution. As low as 0.05ug/mL (1.6 x 10exp-6 M) formaldehyde concentration can be determined, and the linear range was up to 3ug/Ml (1.0exp-4 M). This enzymatic method is simple, sensitive, selective and can be used for the determination of formaldehyde in air, particularly in indoor environments.

52. Fatibello-Filho, O., Suleiman, A. A., and Guilbault, G. G., "Piezoelectric Crystal Sensor for the Determination of Formaldehyde in Air", TALANTA, 38, 541, (1991)

Formaldehyde in air was detected and assayed with a piezoelectric quartz crystal coated with a 7,10-dioxa-3,4-diaza-1,15,12,16-hexadecatetrol/chromotropic acid solution. Water vapor and several gaseous interferents were removed by passing the sampling stream through a column of anhydrous magnesium perchlorate. The response curves were linear in the concentration ranges 0.4-4.5 and 0.4-3.6 ppm v/v CH2O with and without the scrubber column, respectively. A single coating was used for 12 days (500 assays) without significant loss in sensitivity. With a single-point daily recalibration, the useful lifetime of the coating is about 2 months.

53. Septon, J. and Ku, J. C., "Workplace Air Sampling and Polarographic Determination of Formaldehyde", AM. IND. HYG. ASSOC. J., 43, 845, (1982)

A polarographic method has been developed for the determination of formaldehyde in workplace air. Samples are collected in midget fritted glass bubblers containing an aqueous solution of 10% methanol. The collected formaldehyde in the absorbent solution is derivatized with hydrazine reagent to form a formaldehyde hydrazone compound. An aliquot of the resulting solution is analyzed by differential pulse polarography at a dropping mercury electrode. the sample generation system, impinger collection, polarographic analysis, and precision and accuracy data are described. The method was validated over the range of 4.8 to 14.7 ppm, which corresponds to 0.5 to 2 times the (peak) OSHA-PEL for a 30-liter sample at airflow rate of 1L/min. The average recovery was 103%. The pooled coefficient of variation or relative standard deviation was 0.08.

54. Guilbault, G. G., "Determination of Formaldehyde with an Enzyme Coated Piezoelectric Crystal Detector", ANAL. CHEM., 5, 1682, (1983)

Formaldehyde dehydrogenase was placed onto a piezoelectric quartz crystal, together with the cofactors reduced glutathione and nicotinamide adenine dinucleotide; a reversible reaction with formaldehyde occurred in the gas phase, the frequency change of which was directly proportional to the concentration of the aldehyde. Excellent selectivity resulted, with little response to other aldehydes or alcohols (>1000:1 selectivity ratio at 1 and 10 ppm formaldehyde).

55. Ho, M. H., and Samanifar, M., "Spectrophotometric Determination of Formaldehyde by Using Formaldehyde Dehydrogenase", ANAL. CHIM. ACTA, 215, 249, (1988)

A new method for the determination of formaldehyde by using formaldehyde dehydrogenase is described. The method is based on the quantitative oxidation of formaldehyde with oxidized nicotinamide adenine dinucleotide (NAD), in the presence of formaldehyde dehydrogenase, to form the reduced dinucleotide (NADH). This enzyme does not require glutathione as a co-factor and the NADH produced, which is directly proportional to the concentration of formaldehyde in the assay solution, is then measured spectrophotometrically at 340nm. Formaldehyde can be determined in the range 250-666 ppm (1.0exp-5-2.7x10exp-4 M). Optimal conditions and the selectively of this enzyme toward formaldehyde are described.

56. Mohlmann, G. R., "Formaldehyde Detection in Air by Laser Induced Fluorescence", APPLIED SPECTROSCOPY, 39, 98, (1985)

A method is described for the instantaneous concentration measurement of formaldehyde (H2CO) in air by laser-induced florescence of the H2CO(A'A"-X'A1)electronic transition. Concentrations down to about 10ppb can be determined in about 100 seconds without any sample collection, water extraction, or further chemical treatment. The influence of the presence of water vapor and methanol vapor in the air on the accuracy of the method has been investigated. It appeared that if the humidity of the ambient air is not taken into account, the detection limit is about 0.15 ppm H2CO in air: the presence of methanol has no influence on the accuracy.

57. King, W. H. Jr., "Piezoelectric Sorption Detector", ANAL. CHEM., 36, 1735, (1964)

Piezoelectric quartz crystals have long been used as frequency and time standards accurate to 1 part in 10exp8 or better. These stable elements become selective gas detectors when coated with various materials. Crystal coated with gas chromatographic substrates produce gas chromatographic detectors which have several advantages: Sensitivity increases with solute boiling point, detectors can be made selective to compound type and respond in 0.05 second, and the output signal is a frequency which simplifies integration of peak areas and digital presentation of data. The crystals used in this work were quartz plates 1/2 inch in diameter, 7.3 mils thick, that vibrate at 9

Mc. a readily measured signal of 1 c.p.s. corresponds to a weight increase of about 10exp-9 gram. coated-crystal moisture detectors sensitive to 0.1 ppm are now commercially available. Hydrocarbon detectors sensing as little as 1 ppm of xylene have been tested.

58. Igawa, M., Hoffmann, M. R., "Active Transport of Formaldehyde Through an Anion-Exchange Membrane Via the Formation of Bisulfite Adduct", CHEMISTRY LETTERS, 597, (1988)

Formaldehyde reacts with bisulfite to form hydroxymethanesulfonate, which is a conjugate base of a strong acid, and is able to be transported actively by the countertransport of hydroxide ion through an anion-exchange membrane. The permeation rate is controlled by pH and formaldehyde can be separated readily from other types of organic solutes via this method.

59. Miksch, R., and Anthon, D. W., "A Recommendation for Combining the Standard Analytical Methods for the Determinations of Formaldehyde and Total Aldehydes in Air", AM. IND. HYG. ASSOC. J., 43, 362, (1982)

Inspection of the Chemistry underlying the MBTH method suggested that the chromotropic acid method might be successfully applied to MBTH containing samples, provided that the MBTH did not act as an interferent. We applied the recommended chromotropic acid method to water and 0.05% MBTH impinger solutions from parallel sampling trains at six field sites, and found the mean formaldehyde levels to differ on the average by 5%. Having established that a single MBTH sample can yield both the formaldehyde and total aliphatic aldehyde contents of a sampled atmosphere we devised a combined method with improved techniques to streamlined laboratory analysis by maximizing procedural overlap.

60. Shirtliffe, C., Rousseau, M. Z., Young, J. C., Sliwinski, J. F., and Sim, P. G., "Formaldehyde Measurements in Canadian Homes Using Passive Dosimeters", FORMALDEHYDE: ANALYTICAL CHEMISTRY AND TOXICOLOGY, American Chemical Society, CH. 12, (1985)

Formaldehyde dosimeters have been tested in urea-formaldehyde foam insulated Canadian homes in which formaldehyde levels range from 0.02 to 0.2 ppm. Performance of commercial and experimental passive dosimeters was evaluated over 2- to 4- and 7- day exposures. Effects of transport, storage humidity and air velocity on blanks and overall performance were investigated. Modifications have improved reproducibility and blanks. Changes have involved design, handling, removal of contamination, and production control. The changes have resulted in the precision of dosimeters becoming almost equal to that of impingers. Devices under development are discussed. Design requirements include precision, accuracy, cost, use by untrained personnel, and blanks. Design requirements identified in the work for low level dosimeters are discussed. Studies and the types of devices used in each are tabulated.

61. Levin, J. O., Anderson, K., Lindahl, R., and Nelson, C. A., "Determination of Sub-Part-per Million Levels of Formaldehyde in Air Using Active or Passive Sampling on 2,4-Dinitrophenylhydrazine-Coated Glass Fiber Filters and High-Performance Liquid Chromatography", ANAL. CHEM., 57, 1032, (1985)

Formaldehyde is sampled from air with the use of a standard miniature glass fiber filter impregnated with 2,4-dinitrophenylhydrazine and phosphoric acid. The formaldehyde hydrazone is desorbed from the filter with acetonitrile and determined by high performance liquid chromatography using UV detection at 365 nm. Recovery of gas- phase-generated formaldehyde as hydrazone from a 13 mm impregnated filter is 80-100% in the range 0.3-30ug of formaldehyde. This corresponds to 0.08-8.3 ppm in a 3 L air sample. When the filter sampling system, is used in the active mode, air can be sampled at a rate of up to 1 l/min, affording an overall sensitivity of about 1 ppb based on a 60 L air sample. Results are given from measurements of formaldehyde in indoor air. The DNP coated filters were also evaluated for passive sampling. In this case 37 mm standard glass fibers were used, and the sampling rate was 55-65 ml/min in two types of dosimeters. The diffusion samplers are especially useful for personal exposure monitoring in the work environment.

62. Mulik, J. D., Lewis, R. G., and McLenny, W. A., "Modification of a High Efficiency Passive Sampler to Determine Nitrogen Dioxide or Formaldehyde in Air", ANAL. CHEM., 61, 187, (1989)

This technical note describes the modification of the PSD by replacing the granular sorbent with filter paper treated with appropriate reagents to trap nitrogen dioxide or formaldehyde.

63. Godish, T., "Residential Formaldehyde Sampling- Current and Recommended Practices" AM. IND. HYG. ASSOC. J., 46, 105, (1985)

The usefulness of test results in assessing the health hazard potential of residential formaldehyde exposures depends in great measure on the accuracy and reliability/analysis methods employed, the protocol used in collecting samples, sampling objectives, and an understanding of residential formaldehyde dynamics and their relationship to environmental variables. Active sampling and analysis methods including tubes, the impinger/chromotropic acid method, the impinger/pararosanaline method, and the CEA continuous monitor are reviewed as to advantages and limitations for residential sampling. Passive dosimeter methods including the Dupont Pro-Tec Badge, 3M Monitor, Air Quality Research, Inc. Passive Formaldehyde Kit, and

Envirotech Inc. Dosimeter are also reviewed. Sampling considerations for one time formaldehyde sampling using the impinger/chromotropic acid method are discussed in detail, including pre-sampling closure of residences, maintenance of a standard indoor temperature both before and during sampling, the undesirability of sampling during cold, dry winter weather, sample number, sampling location, height and duration, environmental measurements during sampling, source identification and sample storage, A model formaldehyde sampling protocol based on the impinger/chromotropic acid method is described.

64. Hauser, T. R., and Cummins, R. L., "Increased Sensitivity of 3-Methyl-2-Benzothiazolone Hydrazone Test for Analysis of Aliphatic Aldehydes in Air", ANAL. CHEM., 36, 679, (1964)

A modification of the MBTH procedure is described in which the addition of sulfamic acid, in oxidizing step of the reaction, gives a solution free of turbidity and capable of colorimetric analysis without dilution by acetone.

65. Sawicki, E., Hauser, T. R., Stanley, T. W., and Elbert, W., "The 3-Methyl-2-benzothiazone Hydrazone Test", ANAL. CHEM., 33, 93, (1961)

This paper describes some of the early tests for aldehydes and the use of MBTH.

66. Venkatasetty, H. V., "Method and Electrochemical Sensor for Sensing Chemical Agents Using Sensing Electrode Coated with Electrically Conductive Polymers", US PATENT 4,662,996

a method of detecting the presence of polar chemical agents or toxic species by means of an electrochemical cell is described.

67. Wohltjen, H., Barger, W. R., Snow, A. W., and Jarvis, N. L., "A Vapour Sensitive Chemiresistor Fabricated with Planar Microelectrodes and a Langmuir-Blodget Organic Semiconductor Film", IEEE TRANSACTIONS ON ELECTRON DEVICES, ED 32, 1170, (1985)

A vapor sensing method has been developed which is compatible with monolithic silicon microelectronics technology. Specifically, electronic conductance changes caused by vapour interactions with thin films of organic semiconductors are shown to be sensitive, reproducible, rapid and stable chemical detectors. Functionalized copper pthalocyanine multilayer films deposited by Langmuir-Blodget technique onto planar microelectrode arrays can easily detect ammonia at sub ppm concentration levels.

68. Janata, J., "Chemical Sensors", ANAL. CHEM., 64, 196R, (1992)

This paper provides a detailed review of chemical sensing methods for gases and vapours.

69. Katritsky, A. R., and Offerman, R. J., "The Development of New Microsensor Coatings and a Short Survey of Microsensor Technology" ANAL. CHEM., 21 , 83, (1989)

This review covers microsensor coatings for use on surface acoustic wave (SAW) devices for frequency and resistance based measurements. These devices are sensitive to gases, vapours and dusts and much of the work on coatings focuses on making the devices selective, quantitative, sensitive, reproducible and reliable.

70. Morrison, S. R., "Semiconductor Gas Sensors", SENSORS AND ACTUATORS, 2, 329, (1982)

The various ways that gaseous species can affect the resistance of a semiconductor are discussed, with particular emphasis on those where the effect is reversible and, hence, suitable for gas sensing. These latter include reduction/ oxidation of the semiconductor, anion exchange with the semiconductor, adsorption directly on the semiconductor and adsorption by reaction with a surface state. The requirements on the semiconductor are discussed, and it is concluded that oxide semiconductors are usually required. Means to increase the sensitivity and specificity of the gas sensor are discussed , including the form of the semiconductor, catalysts and intentionally added surface states.

71. Guilbault, G. G., and Jordan, J. M., "Analytical Uses of Piezoelectric Crystals: A review", CRC CRITICAL REVIEWS IN ANALYTICAL CHEMISTRY, 19, 1, (1988)

This review describes the use of piezoelectric crystals as sensors. Water vapor detection, gas chromatography detection, liquid chromatography detection. The quartz crystal microbalance, particulate mass concentration detection, trace metal analysis, specific gas detection including formaldehyde, solution measurements, and commercially available instrumentation are described.

72. Santry, S. J., and Walsh, P. T., "Eight-Hour TWA Personal; Monitoring Using A Diffusive Sampler and Short Term Stain Tube", AM. IND. HYG. ASSOC. J., 48, 287, (1987)

A simple technique is described which allows the use of readily available short term stain tubes for 8-hr monitoring. The 8-hr sample is collected on a diffusive sampler and subsequently thermally desorbed through the appropriate stain tube.

73. Gammage, R. B., and Hawthorne, A. R., "Current Status of Measurement Techniques and Concentrations of Formaldehyde in

Residences", FORMALDEHYDE: ANALYTICAL CHEMISTRY AND TOXICOLOGY, CH. 9, American Chemical Society, (1985)

For measuring concentrations of formaldehyde in residences, scientists are making increasing use of passive integrating monitors that provide time weighted average concentrations down to slightly more than 0.1 ppm if the periods of exposure are extended to a few days. The more traditional modified NIOSH method with a 12-2 hour sampling time lacks the sensitivity to make accurate measurements at the frequently encountered concentrations of 0.1 ppm or lower. More rigorous intercomparisons of various monitoring systems are required. Marked dependence of formaldehyde concentrations on age is observed for different classes of dwellings. As building and furnishing materials that contain urea-formaldehyde resins age they emit formaldehyde less strongly. Limited studies have revealed diurnal and seasonal within-house fluctuations of two and tenfold, respectively. Occasional excursions to 0.1 ppm seem to occur in the majority of houses.

74. Light, E. N. "Evolution of Testing Methodology for Atmospheric Formaldehyde in the Home Environment", FORMALDEHYDE :ANALYTICAL CHEMISTRY AND TOXICOLOGY, CH. 6, American Chemical Society, (1985)

Unique requirements of residential formaldehyde sampling programs include a low limit of detection, an averaging time comparable to suspected dose-response relationships, a consideration of environmental factors that determine indoor air quality, and the need for simple, low cost screening techniques. NIOSH P@ CAM 125 and passive dosimeters have been the most commonly used home sampling methods. Accuracy of these tests is subject to a variety of limitations. Meteorological and occupant related factors cause significant fluctuations in home formaldehyde levels. Standard test conditions involving temperature, ventilation, and transient sources have been developed. Models for the adjustment or interpretation of home test results are also in use. Health assessments of measured residential formaldehyde levels have included a 0.1 ppm guideline, a generalized statement of risk, and site specific medial diagnoses.

75. Miller, H. H., and Hirshfeld, T. B., "Fiber Optic Sensors for Industrial and Process Control", PROC. SPIE-INT. SOC. OPT. ENG., 718, (1987)

Fiber optic sensors have been developed for monitoring in plant gaseous emissions of NH3, Formaldehyde, H2S, CO2, O, and NO2. Some of the sensors are reversible and are engineered to remain in place for periods up to one year. Others require replacement every couple of days.

76. Roberts J. M., "Automated Fluorometric Determination of

Formaldehyde in Air", CHEMTRACTS: ANAL. PHYS. CHEM., 1, 53, (1989)

Ambient air is sampled through a glass coil to which a small stream of Ph 2.0 aq. soln. of HCL is added. The resulting solution containing formaldehyde hydrate is mixed with solutions containing NAD (NAD+) and formaldehyde dehydrogenase, which results in the formation of fluorescent NADH. Continuous fluorometric detection of NADH is accomplished at excitation and emission wavelengths of 340 and 460 nm resp.

77. Guilbault, G., Ngeh-Ngwainbi, J., Foley, P., and Jordan, J., "Use of Protein Coatings on Piezoelectric Crystals for Assay of Gaseous Pollutants", ANAL. CHEM. SYMP. SER., 25, 335, (1986)

The use of antibody and enzyme containing protein coatings on piezoelectric crystals for the assay of gaseous pollutants provides parts per billion sensitivity, response times <1 minute and excellent stability of the coatings.

78. Omerzu, S., Hartung, J., and Schuetz, M., "Bacterial Bioluminescence as Indicator for Air Pollutants", DECHEMA BIOTECHNOLOGY CONF., 4, 517, (1990)

The light output of Photobacterium Phosporeum is increased by gaseous pollutants. A simple small assay, application and procedure were developed for air analysis using surface cultures. The minimum effective concentrations determined using this biological indicator are HCHO 20 ppm; SO2 3 ppm.

79. Fortmann, R. C., Rector, H. E., and Nagda, N. L., "Evaluation of Passive Monitors for Measuring Indoor Radon and Formaldehyde" REPORT EPRI-EM-6122, Palo Alto California, (1988)

The performance of passive HCHO and Rn monitors was evaluated by testing under natural conditions in 2 well instrumented research houses and under highly controlled conditions in a radon exposure chamber. Rn monitors evaluated include alpha track detectors, charcoal canisters, and electret radon monitors. A passive diffusion tube monitor for HCHO was evaluated. All 3 passive Rn monitors were < +/-25%. In most cases, measurement errors with the passive radon monitors were <+/-15%. Precision of the monitors was good, generally <+/- 10%. Performance of the passive HCHO monitors was marginal when duplicate monitors were deployed; triplicate monitors were required to obtain acceptable accuracy. Test results demonstrated that the passive Rn monitors are well suited for utility sponsored measurement programs and for use by homeowners. To obtain optimal performance with passive monitors, quality assurance programs need to be implemented to address sampling duration, deployment procedures, handling and storage, anal., and interferences, like water vapour adsorption by charcoal canisters. Continued experimental testing and evaluation of new passive measurement technologies, including the electret radon monitors, is recommended because of the potentially widespread use of passive monitors for indoor measurements.

80. "ASTM D5221 Standard Test Method for Continuous Measurement of Formaldehyde in Air", Section 11.03, Annual Book of ASTM Standards, (1992)

This test method covers the continuous measurement of formaldehyde vapor in indoor or outdoor atmospheres. The commercial analyzer (CEA Instruments; model TGM 555) has been modified such that formaldehyde vapor is absorbed in acidified (HCL) pararosanaline with subsequent addition of dilute sodium sulfite. The resultant coloured product has a strong absorption band in the visible region (530 to 600 nm). The test method is applicable to concentrations of formaldehyde from 0.008 to 0.5 ppm. Detection limits are dependent on sample airflow rate.

81. "ASTM D5197 Standard Test Method for Determination of Formaldehyde and other Carbonyl Compounds in Air (Active Sampler Methodology)" Section 11.03, Annual Book of ASTM Standards, (1992)

This test method covers a procedure for the determination of formaldehyde (HCHO) and other aldehydes in air. This test method is specific for formaldehyde but, with modification, fourteen other aldehydes can be detected.

This method involves drawing air through a cartridge containing silica gel coated with 2,4 dinitro-phenylhydrazine (DNPH) reagent. Aldehydes and ketones readily form a stable derivative with the DNPH reagent. The DNPH derivative is analyzed for aldehydes and ketones utilizing high performance liquid chromatography (HPLC). The sampling procedure is a modification of U.S. EPA Method TO-11.

The sampling method gives a time weighted average. It can be used for long term (1-24 h) or short term (5 to 60 min) sampling of indoor air for formaldehyde. The sampling flow rate is presently limited to about 1.5 l/min. This limitation is presently due to the high pressure drop across the cartridges.

82. "ASTM D5014-89 Standard Test Method for Measurement of Formaldehyde in Indoor Air (Passive Sampler Methodology)", Section 11.03, Annual Book of ASTM Standards, (1992)

This test method covers personal or area measurements of formaldehyde in indoor air in the range from 0.025 to 14 ppm. Formaldehyde is collected in a passive diffusion sampler, and analyzed by a colorimetric method using 3-methyl-2-benzothiazoline hydrazone hydrochloride (MBTH). The recommended sampling time is 15 min to 8 h.

Formaldehyde is absorbed into a 0.05% aqueous solution of MBTH contained in a sampler consisting of a glass vial with a septum cap that retains a Knudsen disc. During air sampling the disc is inverted to establish contact between the absorbing solution and the disc. Formaldehyde passes from the ambient atmosphere into the MBTH solution through the disc at a constant rate.

After collection, the resulting azine is oxidized by ferric chloride sulfamic acid solution to from a blue cationic dye in acidic medium. The concentration is determined by colorimetry at 628 nm.

83. "USEPA Method 1P-6A: Determination of Formaldehyde and other Aldehydes in Indoor Air Using a Solid Adsorbent Cartridge; Compendium of Methods for the Determination of Air Pollutants in Indoor Air", USEPA (1989)

This method describes a procedure for determination of Formaldehyde and other aldehydes in indoor air. The method is specific for formaldehyde, but with modification, fourteen other aldehydes can be detected.

The method is based on the specific reaction of carbonyl compounds with DNPH coated cartridges in the presence of an acid.

A known volume of indoor air is drawn through a prepacked silica gel cartridge coated with acidified DNPH at a sampling rate of 500-1200 Ml/min for an appropriate period of time.

After sampling the formaldehyde is extracted from the cartridges with acetonitrile and analyzed by isocratic reverse phase HPLC which employs a UV detector with an absorption at 360 nm.

The method is described in detail.

84. "USEPA Method 1P-6B: Determination of Formaldehyde and Other Aldehydes in Indoor Air Using a Continuous Colorimetric Analyzer; Compendium of Methods for the Determination of Air Pollutants in Indoor Air", USEPA (1989)

This method describes a procedure for indoor air sampling and analysis of formaldehyde. The procedure employs an automated wet chemical colorimetric analyzer (CEA Instruments, Inc; TGM 555-FD)

The analyzer is fully portable and can be placed on a tabletop or other appropriate surface for monitoring formaldehyde in indoor air.

The lower quantification limit of the MBTH test method is 0.03 ug per millilitre of absorbing solution used. A formaldehyde concentration of 0.025 ppm can be determined in indoor air, based on using an aliquot of 5 Ml of absorbing solution in the prescribed sampler for a period of 8 h and observing a minimum difference of 0.05 absorbance units from the blank when using spectrophotometer cells of path length 1 cm.

Water soluble aliphatic aldehydes give a positive interference

85. "USEPA Method 1P-6C: Determination of Formaldehyde and other Aldehydes in Indoor Air Using Passive Sampling Device; Compendium of Methods for the Determination of Air Pollutants in Indoor Air", USEPA (1989)

The passive sampling method involves loading 2,4-dinitrophenylhydrazine on glass fiber filters and placing them behind sets of diffusion barriers on each side of a containment cavity of a PSD.

Formaldehyde and other aldehydes diffuse to the PSD and react specifically with the DNPH treated filters in the presence of an acid to form a stable DNPH-derivative according to Ficks first law of diffusion.

After sampling the PSD is capped, returned to the laboratory, disassembled under a nitrogen blanket, extracted with acetonitrile and analyzed by high performance liquid chromatography.

This procedure claims to measure formaldehyde below 0.1 ppm in several hours whereas other passive methods require much longer periods.

86. Lodge, J. P., "Intersociety Method 117; Formaldehyde-MBTH Method", "METHODS OF AIR SAMPLING AND ANALYSIS", (1990)

This method involves active sampling with impingers followed by offsite analysis.

An air sample is drawn by means of a portable pump through approximately 35 ml of MBTH solution at a flow rate of 0.5 L/min. A solution of ferric chloride-sulfamic acid is added and the absorbance measured at 628 nm.

The sensitivity of the method is 0.03 ppm for a 25 L sample.

87. "Modified NIOSH Method", NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH MANUAL OF ANALYTICAL METHODS, 2nd edition, Taylor, D. G. Ed., NIOSH, Cincinnati, Ohio, (1977), Vol. 1, Publication 77-157-A, P& CAM 125. Also NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH MANUAL OF ANALYTICAL METHODS, Taylor, D. G. ED., NIOSH, Cincinnati, Ohio, (1981), Vol. 7, Publication 82-100, P& CAM 354

This wet chemical procedure involves active field sampling with off site analysis. Formaldehyde is collected by drawing an air sample at 1 L/Min through a midget impinger containing a small volume (20 ml) of 1% sodium bisulphite solution for periods from 30 min to several hours.

The colour is developed using chromotropic acid and sulfuric acid and the absorbance is read at 580 nm with a colorimeter.

The sensitivity is dependent on the air volume (0.16 ppm for 15L sample, 0.004 for a 60 L sample)

88. R.R. Miksch, D.W. Anthon, L.Z. Fanning; C.D. Hollowell; K. Revzan; J. Glanville; Modified Pararosaniline Method for the Determination of Formaldehyde in Air; ANAL CHEM. 53, 2118, (1981)

This method involves the collection of formaldehyde by means of a small air pump in an acidified solution of pararosaniline.

The absorbance of the coloured solution is measured at 570 nm with a colorimeter.

The sensitivity of the method is related to the volume of the air sample taken and can be as low as 0.005 ppm. Sampling periods of 1 to 8 hours are normally employed.

89. Directory of Instruments and Measurement Methods; Report Submitted to Canada Mortgage and Housing Corporation by Instruscience Ltd., (1991)

This report reviews instruments and measurement methods currently being employed for formaldehyde measurement.

90. Levin, J. O., Lindahl, R., and Anderson, K., "Monitoring of Parts-Per-Billion Levels of Formaldehyde Using a Diffusive Sampler", JAPCA, 39, 44, (1989)

A diffusive sampler for formaldehyde originally designed for use in personal monitoring of worker exposure has been evaluated for static measurement of low formaldehyde levels in indoor air. The sampler consists of a 37-mm glass fiber filter impregnated with 2,4-dinitrophenylhydrazine and phosphoric acid and mounted in a polystyrene filter cassette. Formaldehyde is sampled by controlled diffusion and subsequent hydrazone formation on the filter. The hydrazone is eluted from the filter with acetonitrile and analysed by liquid chromatography and a UV detector. The diffusive sampler was evaluated for static (area) sampling in several industries, offices and homes with formaldehyde levels of 6-200 ppb. Results from diffusive samplers were compared with results from pumped samplers. Even at low wind velocities (<0.01 m/s) there was good agreement between pumped and diffusive samples. The sensitivity will be 1 ppb in a 24-hr sample, making the sampler especially useful for indoor air monitoring of low formaldehyde levels.

91. Stewart, P. A., Cubit, D. A., Blair, A., and Spirtas, R., "Performance of Two Formaldehyde Passive Dosimeters", APPL. IND. HYG., 2-2, 61, (1987)

Two formaldehyde passive dosimeters, the DuPont Pro-Tek(R) badge and the 3M Formaldehyde Monitor 3751, were compared to the NIOSH P&CAM 125 method using t-tests and multvariate analyses. Approximately 270 area samples (90 sets of matched samples) were taken in nine formaldehyde-using plants. Above the level of sensitivity (1.60 ppm-hours), the results of the DuPont badge were, on average, not statistically different from those of the NIOSH method using the t-test. The slope of the fitted linear regression line comparing the DuPont badge results to the NIOSH method results was statistically different from zero, and the coefficient of determination (R2) was 0.92. Above the level of sensitivity (0.80 ppm-hours), the results of the 3M badge were, on average, lower (but not statistically) than those of the NIOSH method. The slope of the fitted regression line was different from zero, and the coefficient of determination was 0.44. The prescence of dust was found to be a significant variable in determining how well each dosimeter predicted the NIOSH method, and after adjusting for dust, both predicted the NIOSH method well.

92. Kring, E. V., Thornley, G. D., Dessenberger, C., Lautenberger, W. J., and Ansul, G. R., "A New Passive Colorimetric Air Monitoring Badge for Sampling Formaldehyde in Air", AM. IND. HYG. ASSOC. J., 43, 786, (1982)

A new diffusion colorimetric air monitoring badge for sampling time-weighted average concentrations of formaldehyde is described. This small, lightweight badge can be used for either personal or area monitoring. Laboratory validation and field test data showing that the badge is both precise and accurate within OSHA and NIOSH limits are included. The badge has a sampling range of 2-55 ppm-hrs, which is sufficient to determine workplace concentrations at both TWA and ceiling levels.

93. Geisling, K. L., Tashima, M. K., Girman, J. R., and Miksh, R. R., "A Passive Sampling Device for Determining Formaldehyde in Indoor Air", ENVIRN. INT., 8, 153, (1982)

A passive sampling device based on the principle of diffusion has been developed for the determination of formaldehyde in ambient air. The sampler consists of a capped glass tube (with approximate dimensions of 2.4 X 9 cm) containing a glass-fiber filter treated with NaHSO3. In the field, the device collects a sample by being uncapped for a specified time. After being recapped and returned to the laboratory, the filter is analyzed by the chromotropic acid (CTA) method. Laboratory validation studies were conducted by exposing the sampling devices for 1 week to dry formaldehyde gas generated by passing trioxane vapor over an acid catalyst bed. In these tests, formaldehyde concentrations ranged from 0.05 to 0.80 ppm. Reproducibility was excellent, with relative standard deviations averaging 5.4% for five constant concentrations. The lower detection limit was determined to be 3.6 ppm. In an occupational environment an 8-h sample would be sufficient to detect compliance with the OHSA permissible exposure limit of 3 ppm; in a residential environment a 1-week sample would allow detection of 0.025 ppm for indoor air quality audits.

94. Kennedy, E. R., and Hull R. D., "Evaluation of the DuPont Pro-Tek(R) Formaldehyde Badge and the 3M Formaldehyde Monitor", AM. IND. HYG. ASSOC. J., 47-2, 94, (1986)

The 3M Formaldehyde Monitor and the DuPont Pro-Tek(R) Formaldehyde Badge were evaluated for performance and reliability. This evaluation revealed that the 3M monitor results were variable and lower than reference concentrations determined independently. When the monitors were humidified before use and then exposed in humid (ca. 80% RH) formaldehyde-containing atmosphere, the monitors did give accurate results. Results of additional experiments led to the conclusion that quantitative reaction between formaldehyde generated in our chamber and the absorbent pad in the 3M monitor required the prescence of a minimum level of absorbed water. The DuPont badges gave good agreement with the reference concentrations determined independently under the following conditions: a) sampling period of 1 to 12 hr with a minimum integrated sample loading of 4 ppm-hr; b) at least 3m/min(10ft/min) face velocity; c) correction for blank badges; and d) correction for loss of reagent from the samples. The evaluation indicated that the DuPont badge was not well suited to short term sampling and was subject to evaporation of liquid from the absorbing blister. Blank values also were found to be variable, necessitating the analysis of several blanks to be used for blank correction with each set of samples. This blank variability also contributed to high variability found when short term measurements were made. The badge also had a negative interference from phenol at high phenol-to-formaldehyde ratios. Some of the major problems observed with both passive monitors were found only after devices which had been aged under storage conditions were analyzed and these results interpreted. If all testing had been done with fresh sampling devices, many of the problems would not have been noticed. Based on the results of this study, this factor of diffusive monitor aging needs to be addressed in any further work on passive monitor evaluation.