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REMOVAL OF IODOMETHANE FROM AIR USING A PILOT-SCALE CORONA DISCHARGE SCRUBBER

ELIMINATION DE L'IODOMETHANE DE L'AIR A L'AIDE D'UN EPURATEUR A DECHARGE CORONA A L'ECHELLE PILOTE

L. W. Dickson, A. Toft-Hall, D. F. Torgerson

Whiteshell Nuclear Research Establishment

Etablissement de recherches nucléaires de Whiteshell

Pinawa, Manitoba R0E 1L0

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L.W. Dickson, A. Toft-Hall and D.F. Torgerson

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ÉLIMINATION DE L'IODOMÉTHANE DE L'AIR À L'AIDE D'UN ÉPURATEUR À DÉCHARGE CORONA À L'ÉCHELLE PILOTE

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RÉSUMÉ

Le présent rapport présente les résultats d'une étude de l'élimination de l'iodométhane de l'air à l'aide d'un épurateur à décharge corona à l'échelle pilote. On a mesuré l'élimination dans les éventails de paramètres suivants: débit de masse d'air, 30 à 350 $m^3 \cdot h^{-1}$; concentration initiale de CH_3I, 6 à 230 $\mu mol \cdot m^{-3}$; courant de décharge, 0 à 75 mA CC (polarité négative). On a éliminé à peu près cinq à dix moles d'iodométhane par mole d'électrons ajoutée au flux d'air à une tension de décharge de ~10 kV. L'efficacité d'élimination laisse supposer que les deux réactions ions-molécules et radicaux-molécules pourraient être importantes dans l'élimination de l'iodométhane de l'air en décharge corona. Les résultats de cette démonstration à l'échelle pilote indiquent qu'un épurateur à décharge corona conviendrait pour l'élimination des espèces d'iode de l'air en tant qu'élément du système d'évacuation, d'urgence d'air filtré d'un réacteur nucléaire. On étudie l'application de cette technologie pour la limitation des émissions d'oxyde d'azote, d'anhydride sulfureux et de sulfure d'hydrogène.

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ABSTRACT

This report presents the results of a study of the removal of iodomethane from air using a pilot-scale corona discharge scrubber. The removal was measured in the following parameter ranges: bulk air flow, 30 to 350 m^3/h; initial CH_3I concentration, 6 to 230 $\mu mol/m^3$; and discharge current, 0 to 75 mA DC (negative polarity). Approximately five to ten moles of iodomethane are removed per mole of electrons added to the air stream at a discharge voltage of $\sim$ 10 kV. This removal efficiency suggests that both ion-molecule and radical-molecule reactions may be important in the removal of iodomethane from air in a corona discharge. The results of this pilot-scale demonstration indicate that a corona discharge scrubber would be suitable for removing iodine species from air as part of the emergency filtered-air discharge system of a nuclear reactor. The application of this technology to the control of nitrogen oxide, sulfur dioxide and hydrogen sulfide emissions is being investigated.

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CONTENTS

1. INTRODUCTION

Airborne radioactive iodine occurs both in organic and inorganic forms. Conventional filtration systems using solid adsorbents remove organic forms from air with relatively low efficiency. Therefore, nuclear off-gas systems require thick filter beds to ensure that all potential chemical forms of radioiodine are immobilized. We have investigated the use of a corona discharge in air as an alternative technology for this application.

A corona discharge is created in the air gap between a sharply pointed electrode and a rounded electrode by applying a high potential across the two electrodes [1]. In the region of large electric field gradient, high-energy electrons ionize and/or excite air molecules, generating a variety of highly reactive species, including oxygen atoms and ions. This highly reactive, oxygen-rich atmosphere is an excellent medium for the oxidation of atmospheric pollutants. Corona discharges have been used to remove hydrocarbons [2,3], methanethiol [3], sulfur dioxide [4,5], methyl parathion [6] and bacteria [6] from air.

Torgerson and Smith [7] demonstrated that a corona discharge can remove both iodomethane and iodobenzene from air with efficiencies greater than 99.9%. The iodine was precipitated as the solid oxides I_2O_4 and I_4O_9 [8]. The applicability of the corona discharge method has also been demonstrated using radioactive iodine both in the laboratory and in the off-gas stream from the ^{99}Mo facility at the Chalk River Nuclear Laboratories [9]. Recent work at the Whiteshell Nuclear Research Establishment has focussed on the elucidation of the chemical reaction mechanism operative in a corona discharge in air- and nitrogen-containing iodomethane at the parts per million level [10,11].

The work described above was performed using corona discharge reactors consisting of an outer tubular electrode at ground potential and an inner wire electrode at a high potential ($\sim$ 10 kV). However, wire electrodes are susceptible to breakage, especially in corrosive environments, and a more compact scrubber is required for large flows. Thus, a more robust corona discharge reactor has been constructed, using the edge of a wire mesh as the high-voltage electrode and a flat plate as the grounded electrode. This new design has also reduced the size of the scrubber unit. The initial results of a study of the removal of iodomethane from air using this scrubber are presented in this report.

2. EXPERIMENTAL

A schematic diagram of the pilot-scale iodine filter test facility is shown in Figure 1. The facility consists of a 300 mm x 300 mm square duct placed inside a fume hood, both of which are connected to the building air exhaust system. The corona discharge scrubber is fitted into a removable section of the duct, as shown in Figure 1. The ranges of operating parameters are as follows:

Flow (F):	30 to 350 m^3/h
Temperature (t):	ambient to 80°C
Relative Humidity (RH):	ambient to 100% .

The air flow is provided by suction from the air exhaust system and is regulated by a damper. Temperatures above ambient are obtained using an intermittent electrical heater controlled by a microprocessor-based temperature controller. The relative humidity of the air stream is changed by steam injection. Stainless steel wire meshes have been inserted into the duct, upstream and downstream of the scrubber, to obtain greater uniformity of CH_3I concentration and air flow velocity.

The air flow rates were calibrated by admitting a known amount of nitrogen dioxide into the air stream through the iodomethane inlet and monitoring the NO_2 concentration as a function of position in the duct in the vicinity of the scrubber. With the present inlet system, the pollutant of interest is premixed with an air flow of about 5 m^3/h, and this stream is injected into the main air flow using a multiple injector inlet about 2 m upstream of the scrubber unit. This method of pollutant injection gave a peak concentration at the center of the duct approximately twice the concentration at the duct walls. For the present work, the volumetric air flow at a given velocity reading on the anemometer was determined by dividing the input challenge of NO_2 by the average of the NO_2 concentrations measured along vertical and horizontal traverses of the duct.

Reproducible iodomethane concentrations were obtained by bubbling nitrogen gas through liquid iodomethane in a constant temperature bath (T_1), and flowing this mixture through a trap in a second constant temperature bath ($T_2 < T_1$), prior to mixing this gas stream with the main air stream. Iodomethane vapour pressures were taken from the work of Wren and Vikis [12]. Iodomethane analyses were performed using a gas chromatograph equipped with a ^{63}Ni electron capture detector. Ozone production was recorded using a commercial ozone monitor based on UV absorption.

The corona discharge scrubber measured 300 mm x 300 mm x 150 mm and consisted of eight gas-flow channels separated by 6-mm-thick grounded copper plates. Each channel contained a row of four high-voltage electrodes. These electrodes were made by soldering a copper mesh (0.18-mm diameter wire, 1 mm spacing) to a stainless steel support rod. The discharge occurred in the 8-mm gap between the edge of the mesh and the neighbouring grounded plate. This gap was kept very uniform (±0.1 mm), to obtain a stable, uniform corona discharge. In the dark, intense discharge points next to the tips of the high-voltage electrodes and luminous zones between the bright points and the grounded electrodes could be observed. These luminous zones were due to emission from reactive species. The iodomethane in the gas stream passes through these zones during its transit of the corona discharge unit and reacts with the active species in the luminous zones, and iodine is directed by the applied potential to the grounded electrodes, where it is trapped. Copper was selected as the electrode material because of its ability to chemisorb iodine.

Acrylic insulators were used for positioning the high-voltage electrodes in the scrubber. Degradation of the insulators in the corona discharge environment, caused by the formation of a conducting film on the

insulators, necessitated cleaning and polishing these insulators about every six months of scrubber operation.

Some short-term hysteresis was noted in the scrubber performance. Larger and more reproducible iodomethane removals and less frequent incidences of arcing were observed when the scrubber was operated at a moderate current ($\geq$ 25 mA) for approximately 0.5 h prior to measuring the removal at lower current. This procedure was carried out at the beginning of each day of experimentation. In addition, the iodomethane removal increased by $\sim$ 1 to 5% for consecutive measurements at a particular current, even after initial operation at higher current. The removals reported here are averages of four measurements of the iodomethane concentration obtained over a period of 1 h of scrubber operation.

3. RESULTS

A typical plot of the decontamination factor (D.F. = initial CH_3I concentration divided by final CH_3I concentration) as a function of discharge current is shown in Figure 2 for the conditions $[CH_3I]_o$ = 230 µmol/m³, F = 32 m³/h, t = 22°C and RH = 9%. The data show an approximately exponential dependence of log D.F. on current. Thus, a small increase in discharge current gave a large increase in decontamination factor. The detection limit of the gas chromatograph was approximately 0.1 µmol/m³ for CH_3I in air and, therefore, the maximum D.F. that could be measured was about 2000.

Figure 3 shows a plot of log D.F. as a function of power dissipated in the scrubber for the same experimental conditions as those of Figure 2. The shapes of the curves in Figures 2 and 3 are quite similar because only a small increase in voltage increases the current substantially (e.g., V = 9.2 kV for I = 2.5 mA, V = 10.2 kV for I = 20 mA). From Figure 3, we see that the dissipation of 205 W in the corona discharge yields a D.F. of 1000 for a challenge of 2×10^{-6} mol/s CH_3I.

Figure 4 shows the effect of iodomethane concentration on scrubber performance. Log D.F. is plotted as a function of current for three values of the initial iodomethane concentration, $[CH_3I]_o$ = 52, 25 and 7 µmol/m³, at F = 280 m³/h and room temperature. Increasing the iodomethane concentration increases the amount of discharge current that must be supplied to obtain large decontamination factors. For an initial iodine concentration of 52 µmol/m³, a discharge current in excess of the capacity of the power supply (75 mA) would have been required to obtain a D.F. of 1000. In the present study, the data were not sufficiently reproducible to permit quantitative data analysis. Hence, further work will be required to determine an expression relating the observed D.F. to the iodomethane concentration, bulk gas flow and discharge current.

The effect of relative humidity on scrubber performance is shown in Figure 5. This series of experiments was performed under the following conditions: $[CH_3I]_o$ = 70 µmol/m³, F = 32 m³/h, t = 45 to 55°C. The current, I = 12 mA, was selected to remove 97 to 99% of the iodomethane.

The figure shows that, under these conditions, removal efficiency is not affected by relative humidities up to 60% (5.7 mol% H_2O in the air stream). Other results show degraded scrubber performance in the presence of wet steam. Previous bench-scale studies have shown that increasing the relative humidity to 97% at room temperature has no effect on the removal of CH_3I from air in a corona discharge [7]. Further work will be necessary to assess the performance of the pilot-scale scrubber at humidity levels approaching saturation.

An experiment was performed to determine the effect of gas temperature on scrubber efficiency. The current required to obtain a given change in CH_3I concentration was independent of temperature, but the voltage required for a given current was lower at higher temperatures (for I = 5 mA, V = 9.7 kV at 22°C and V = 8.5 kV at 55°C). Thus, the power consumption was about 10% lower at 55°C than it was at 22°C.

The ozone concentration was monitored at the outlet of the scrubber. The ozone production was independent of initial iodomethane concentration and fell between 30 and 70 O_3/e^- for most experiments. The ozone production tended toward the upper part of this range at higher flows due to the trade-off between ozone production by $O + O_2 + M \rightarrow O_3 + M$ and decomposition by $O + O_3 \rightarrow 2O_2$ in the discharge region. The maximum ozone concentration observed in the scrubber effluent was about 1000 $\mu mol/m^3$. The maximum concentration recommended for occupational exposure is 40 $\mu mol/m^3$ [13]. Thus, it is necessary to dilute the scrubber effluent in the atmosphere or decompose the ozone in the duct.

The scrubber produces deposits on the grounded electrodes and on the inner surfaces of the duct downstream of the scrubber. Elemental analysis of these deposits by X-ray fluorescence spectroscopy showed the presence of both iodine and copper. X-ray diffraction analysis was not conclusive, but the pattern resembled that of $CuI_{0.4}O_{0.2}(OH)_{1.4} \cdot 0.74H_2O$. The deposit observed in previous bench-scale studies, using a tungsten wire in a tubular stainless steel discharge tube, was identified as an amorphous form of I_4O_9 [8]. The incorporation of copper in the deposit formed in the pilot-scale scrubber is due to reactions of iodine oxides with the copper electrodes, and is desirable due to the lower volatility expected for iodine bound to copper. This erosion of the electrode surface may necessitate periodic electrode replacement. However, operation of the scrubber for six months at relatively high iodomethane concentrations has not resulted in any noticeable degradation of the electrodes.

A bench-scale study of the oxidation of nitrogen dioxide in air using a tubular corona discharge reactor [10,11] has been initiated. Preliminary results show that a corona discharge in humid air converts nitrogen dioxide to nitric acid, indicating that a corona discharge may be used to effect nitrogen oxide removal from flue gases. Future bench-scale studies will focus on the optimization of nitrogen oxide removal efficiency and the applicability of corona discharge gas cleaning technology to other atmospheric pollutants, such as hydrogen sulfide and sulfur dioxide.

4. DISCUSSION

A corona discharge removes approximately five to ten moles of iodomethane per mole of electrons added to the air stream under the conditions investigated here. This efficiency is almost an order of magnitude higher than the efficiency observed for the removal of iodomethane from nitrogen [10]. It is useful to consider some of the chemical reactions that occur in a corona discharge in order to obtain a better understanding of the removal process.

The following reactions are important in the removal of iodomethane from nitrogen [11]:

$$e^-_* + CH_3I \rightarrow CH_3 + I^- \quad (1)$$
$$M^*_* + CH_3I \rightarrow CH_3 + I + M \quad (2)$$
$$CH_3 + I + M \rightarrow CH_3I + M \ . \quad (3)$$

The dissociative electron attachment process (reaction (1)) is most efficient at low electron energies (0.15 ± 0.10 eV) [14]. The neutral dissociation reaction (2) may be effected by either energetic electrons or metastable forms of nitrogen. The importance of reaction (3) depends on its rate relative to that of the recombination of methyl radicals to produce ethane. The overall removal of low concentrations of iodomethane from nitrogen ($\leq$ 1000 μmol/m^3) is primarily due to reaction (1), since most of the iodomethane destroyed in reaction (2) is reformed in reaction (3). Reference [11] contains a detailed model of the decomposition of iodomethane in nitrogen.

The chemistry of corona discharges in air is more complicated than in nitrogen, due to the reactions of oxygen-containing species, such as oxygen negative ions, atomic oxygen, ozone, excited states of oxygen and hydroxyl radicals. The mechanism of CH_3I removal from air in a corona discharge is not fully understood, but the following reactions are thought to be of primary importance:

$$O^-_* + CH_3I \rightarrow CH_3 + IO^- \quad (4)$$
$$M^*_* + CH_3I \rightarrow CH_3 + I + M \quad (5)$$
$$O + CH_3I \rightarrow CH_2I + OH \quad (6)$$
$$OH + CH_3I \rightarrow CH_2I + H_2O \ . \quad (7)$$

Reaction (4) is analogous to reaction (1), but the drift velocity of O^- is much lower than that of e^-, thereby making its lifetime in the air stream longer and increasing the probability of reaction. Ionic chain reactions are probably not significant; thus, reaction (4) can give a maximum removal of one CH_3I per electron. Therefore, neutral reaction paths must be responsible for observed removals in excess of one CH_3I per electron. Reactions (2) and (5) are identical. Deactivating agents reduce the contribution of reaction (5) to the observed removal of CH_3I from air. However, carbon dioxide and other common constituents of air do not appear to reduce the efficiency of CH_3I removal in a corona. Recombination reactions, such as reaction (3), are probably not important since radical species are effectively scavenged by the oxygen in the air. The deactivation of energetic nitrogen and oxygen molecules in air containing water

vapour produces hydroxyl radicals and excited atomic oxygen. These species then react with iodomethane, as shown in reactions (6) and (7). Although ground-state oxygen atoms and ozone are formed in the discharge, their reactions with iodomethane are relatively slow and, thus, are not expected to contribute significantly to the observed iodomethane removal. Further work at a fundamental level is necessary to elucidate the mechanism of this removal process.

Iodine concentrations in the atmosphere of a reactor containment building in an accident situation are expected to be less than 4×10^{-9} mol/m^3 I [15]. The outward air flow through the emergency filtered-air discharge system would be between 100 and 5900 m^3/h, depending on the details of the accident scenario. These values yield a maximum challenge to the filter system of 2.3×10^{-5} mol/h I. The challenges studied in this work are in the range 4.4×10^{-4} mol/h to 1.4×10^{-2} mol/h. Thus, the present scrubber size would probably be adequate for this application. However, further experiments on a full-scale system will be necessary to demonstrate the performance of the scrubber at higher air flows and lower iodine concentrations.

5. CONCLUSIONS

This pilot-scale study of the removal of iodomethane from air using a corona discharge scrubber has demonstrated the applicability of corona discharge technology to airborne radioiodine control. The technique appears to have several advantages over other methods used in the safety systems of nuclear reactors. The corona scrubber unit is approximately an order of magnitude smaller in size than comparable thick adsorbent bed filters. Previous bench-scale work [7,9] has shown that the corona discharge scrubber removes iodomethane, iodobenzene and elemental iodine with similar efficiency. The pressure drop across a corona discharge scrubber is quite low, since the important reactions occur in the gas phase rather than at the gas-solid interface, as is the case with filters based on adsorption. Very large decontamination factors can be attained with the corona discharge scrubber simply by increasing the discharge current. As with impregnated charcoal adsorbents, particulate filters must be incorporated into the air-cleaning system both upstream and downstream of a corona discharge scrubber.

Preliminary experiments have shown that there is potential for a nitrogen oxide scrubber based on corona discharge technology.

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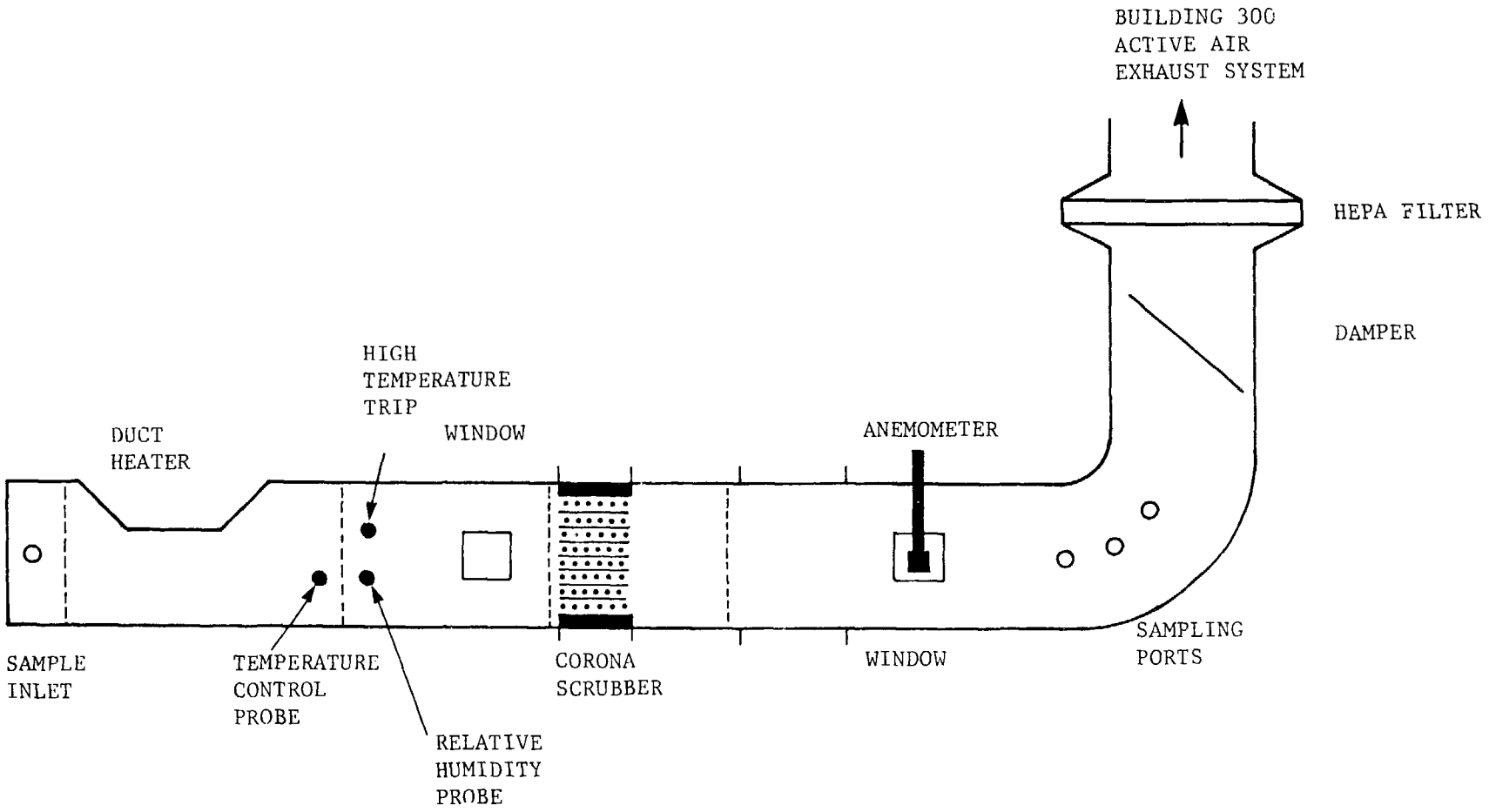

FIGURE 1: Layout of the Pilot-Scale Iodine Filter Test Facility

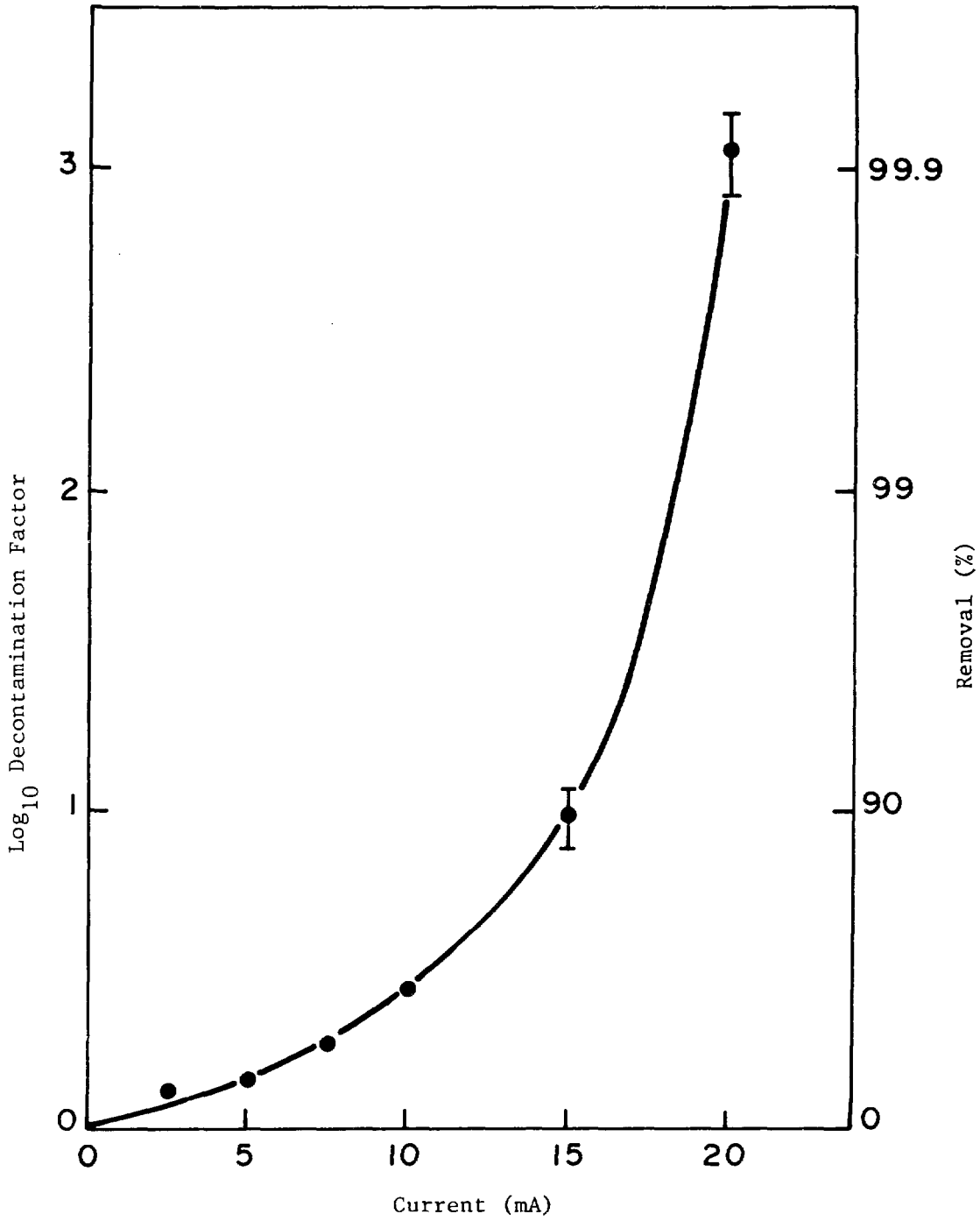

FIGURE 2: Logarithm (base 10) of the Decontamination Factor as a Function of Discharge Current for the Removal of Iodomethane from Air Using the Pilot-Scale Corona Discharge Scrubber. $[CH_3I]_o$ = 230 $\mu mol \cdot m^{-3}$, F = 32 $m^3 \cdot h^{-1}$, t = 22°C and RH = 9%.

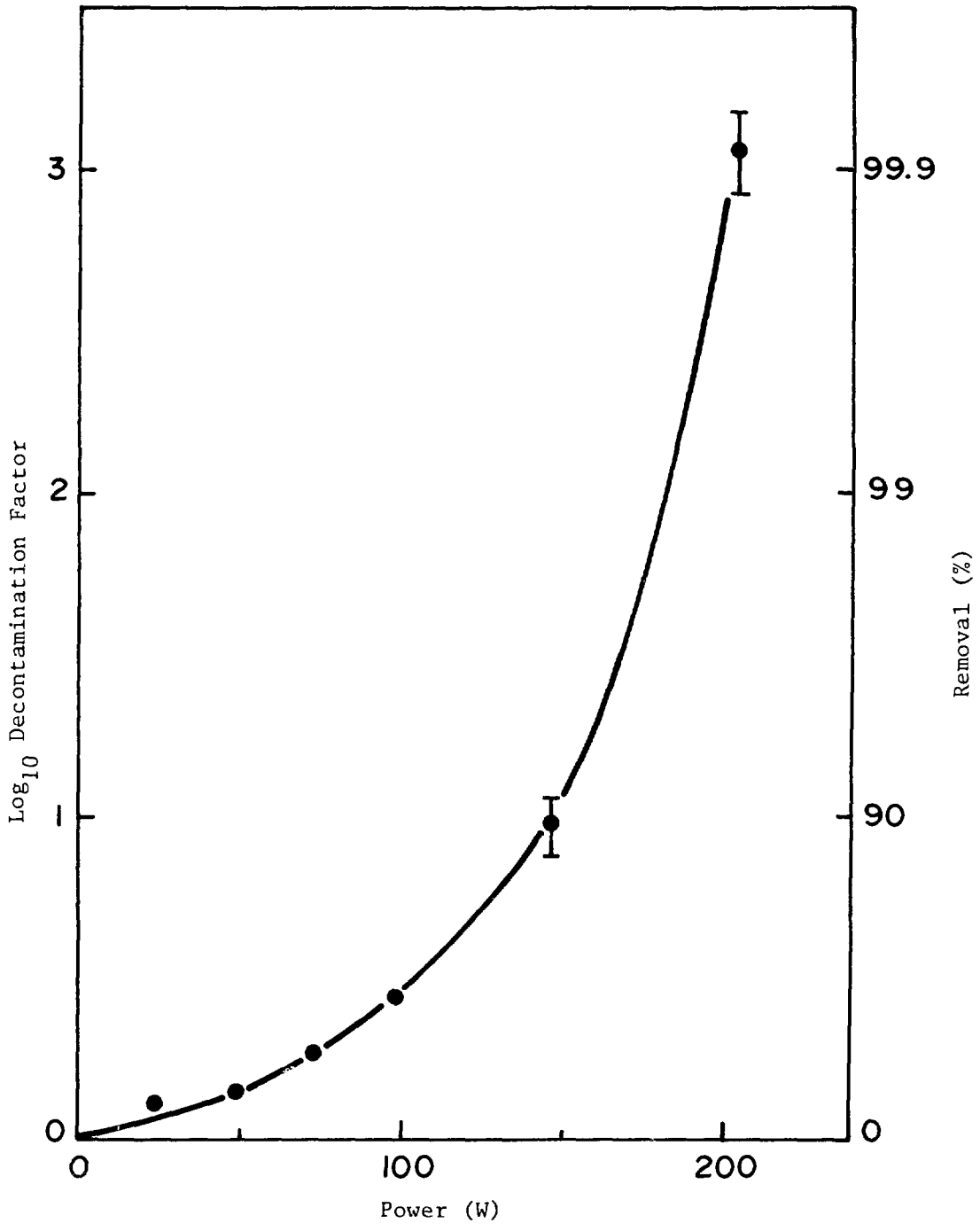

FIGURE 3: Logarithm (base 10) of the Decontamination Factor as a Function of Discharge Power for the Removal of Iodomethane from Air Using the Pilot-Scale Corona Discharge Scrubber. Experimental conditions, as for Figure 2.

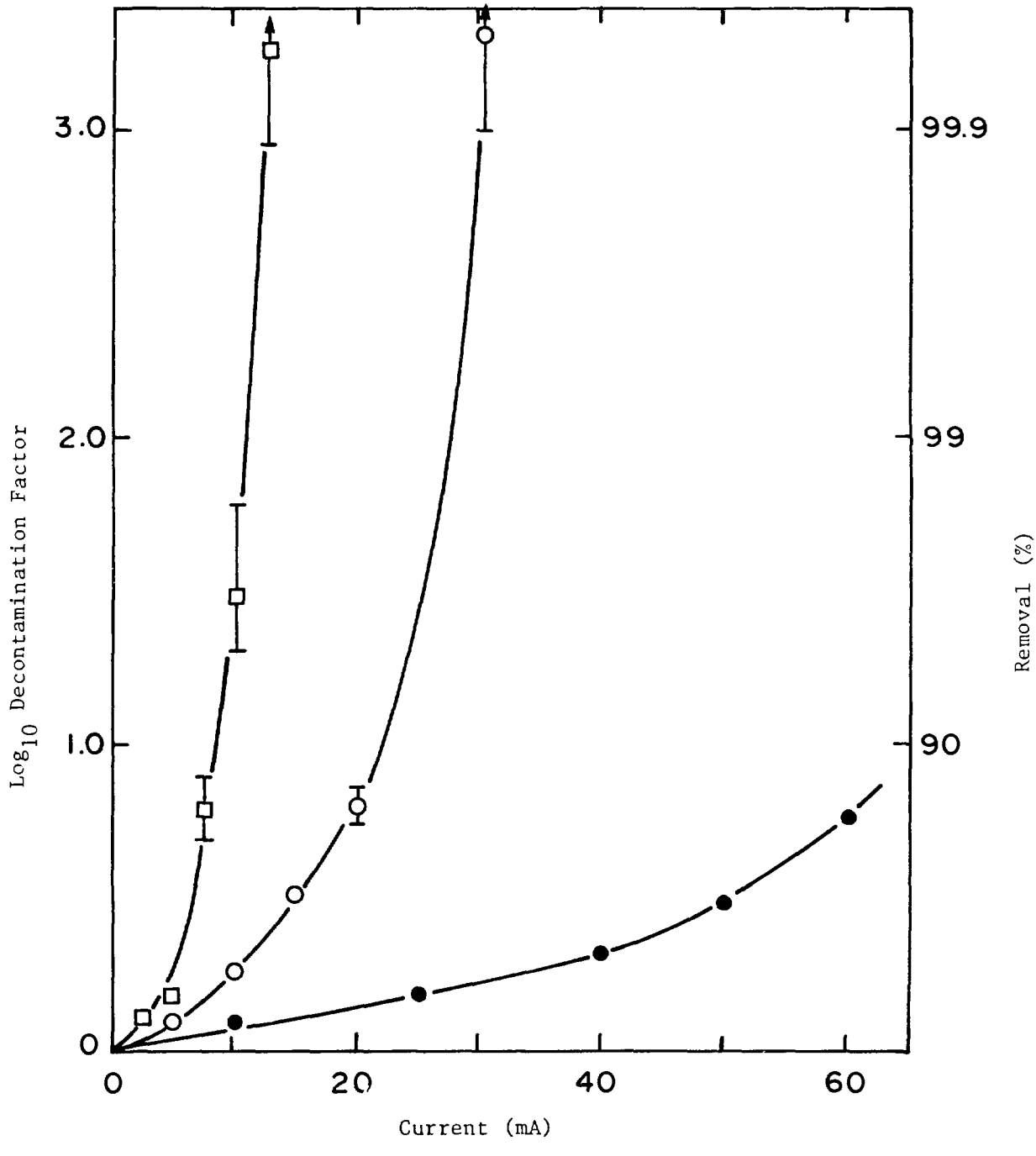

FIGURE 4: Corona Discharge Iodomethane Removal as a Function of Discharge Current at F = 280 $m^3 \cdot h^{-1}$ and room temperature.
● $[CH_3I]_o$ = 52 $\mu mol \cdot m^{-3}$;
○ $[CH_3I]_o$ = 25 $\mu mol \cdot m^{-3}$;
□ $[CH_3I]_o$ = 7 $\mu mol \cdot m^{-3}$.

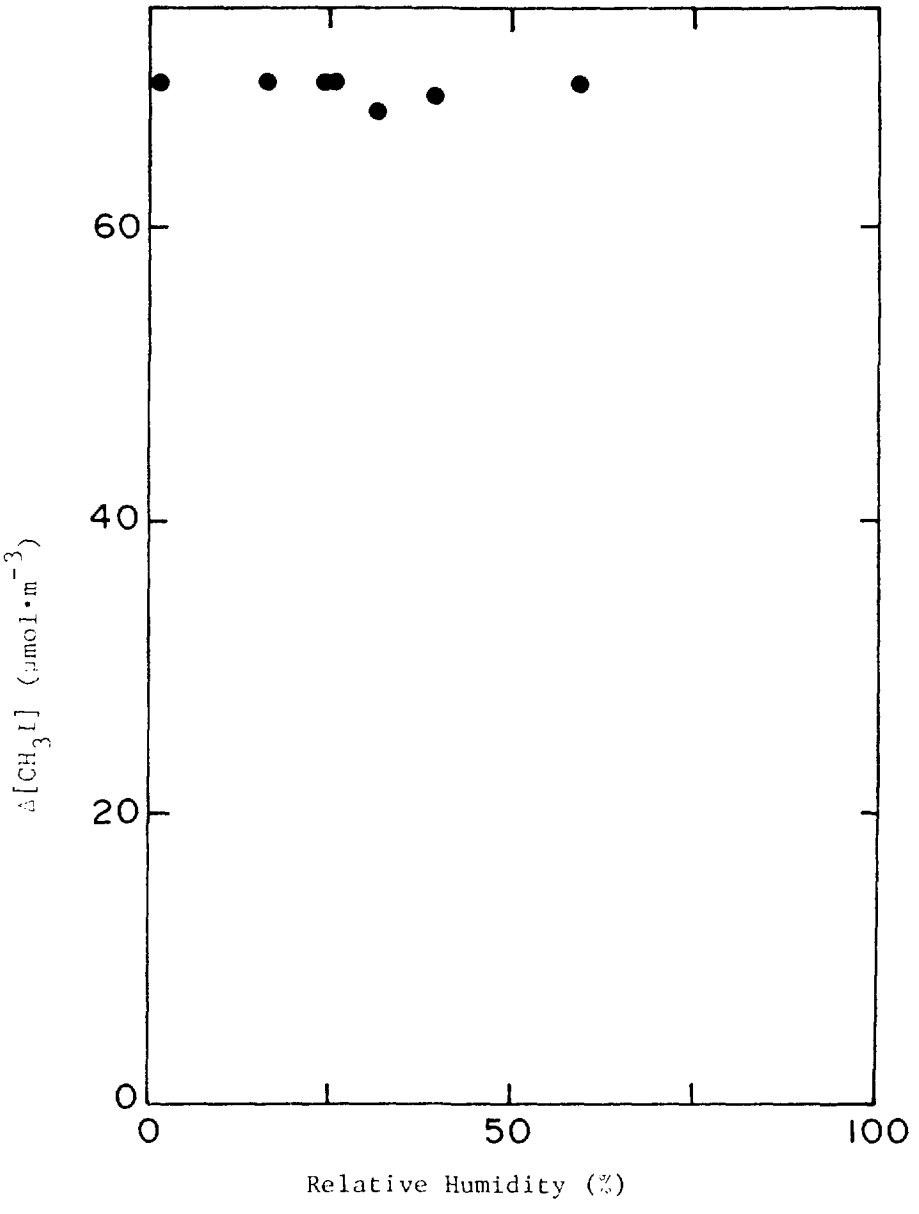

FIGURE 5: Effect of Relative Humidity on Scrubber Performance. $[CH_3I]_o$ = 70 $\mu mol \cdot m^{-3}$, F = 32 $m^3 \cdot h^{-1}$, t = 45 to 55°C and I = 12 mA.

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