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Removal of Trimethylamine and Ammonia Using Electron Attachment Reaction

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ABSTRACT Experimental investigation on the application of electron attachment reaction to the removal of dilute gaseous pollutants has been carried out using a corona-discharge reactor. The effects of several factors, namely, discharge current and coexisting O_2 or H_2O vapor on individual removal efficiency of two kinds of gaseous pollutants, namely, trimethylamine ($(CH_3)_3N$) and ammonia (NH_3) have been investigated. The role of ozonation reaction is next investigated using two reactors in series. In addition, a two-reactor system is proposed and shown to remove both $(CH_3)_3N$ and SO_2 with less by-products. The experimental results reveal that generally the higher the discharge current, the higher the removal efficiency. It is found that the presence of O_2 enhances the removal efficiency of both impurity gases. On the other hand, the presence of water vapor enhances the removal efficiency of $(CH_3)_3N$ but retards that of NH_3.

KEYWORDS: gas purification, electron attachment, corona-discharge reactor, trimethylamine, ammonia.

INTRODUCTION

Removal of dilute malodorous gases has both environmental and industrial significance. Like most countries, Thailand has been facing many environmental problems associated with the unceasing growth of human activities. For instance, the heavy concentration of vehicles in Bangkok leads to serious deterioration in air quality because of heavy automobile emissions. Recently, a latent source of public nuisance emitted from the crematory furnace of a temple has become prominent. Besides particulates, malodorous gaseous components are emitted during cremation, causing frequent complaints from surrounding communities. This is because exhaust gas is directly released to the atmosphere from the stack without any treatment. Malodorous and even noxious gases, such as trimethylamine, ammonia, acetaldehyde and styrene, are produced during cremation.[1] Often their concentrations are diluted with fresh air down to several tens or hundreds of ppm before leaving the stack. Out of the more than 30,000 temples all over Thailand, only a few big ones in Bangkok employ some sort of emission control devices, mainly, the conventional after-burning chamber. A good crematory furnace system is usually imported and costs 6-7 million baht nowadays. From our on-site surveys at a number of temples, the locally made after-burning systems are too small, resulting in inadequate residence time, and their operating temperatures are too low at 550~650°C. Because of greater public awareness and concern on air quality, the removal of malodorous gases from crematory emission has become a national issue.

The new concept of gas purification by low-energy electron attachment was first proposed by Tamon *et al.*[2] When low-energy electrons collide with gas molecules, some of them are captured by the molecules and negative ions are formed. This phenomenon is called "electron attachment"[3] and it depends on the electron energy, the structure of the gas molecule, and its electron affinity. There is a huge difference in the attachment probability among different types of gas molecules, and this leads to high selectivity in the production of negative ions.[3-4] Hence electronegative impurities of extremely low concentration can selectively become negative ions by electron attachment and they can effectively be separated from the neutral gas in an electric field.

Tamon *et al*[2] constructed two kinds of separation devices using either photocathode or glow discharge as electron source. They reported high efficiency for the removal from nitrogen of SF_6 of very low concentrations. Recently Tamon *et al*[5] used two types of corona-discharge reactors to remove sulfur compounds, iodine and oxygen from nitrogen. They also discussed the purification mechanism and presented simulation models for predicting the removal efficiency. Subsequently, Tamon *et al*[6] investigated the influence of coexisting oxygen and/or water vapor on the removal of several sulfur compounds. As a continuation, Sano *et al*[7] used a new type of corona-discharge reactor, the wetted-wall reactor, and the conventional deposition-type reactor to remove iodine and methyl iodide from nitrogen.

Since most malodorous components in crematory emission are highly electronegative, electron attachment should be one promising method to remove them in an electric field. The present work aims at a basic study on the application of electron attachment reaction to the treatment of crematory emission. What follows is an experimental study on the individual removal efficiency of two common components (trimethylamine and ammonia) found in crematory emission. More specifically, the influences of several important factors, namely, discharge current, gas flow rate, inlet gas concentration and major coexisting components in the combustion gas (*ie*, oxygen, water vapor and sulfur dioxide) on the removal efficiency were examined experimentally. During the removal of trimethylamine from oxygen and nitrogen mixed gas, we also confirmed the role of ozone in its removal. An analysis of the reaction by-products was also carried out. In addition, a two-reactor system was proposed and shown to concurrently remove both $(CH_3)_3N$ and SO_2 well with less by-product formation.

MATERIALS AND METHODS

Removal experiments

Fig 1 shows a schematic diagram of the experimental apparatus. A brass tube with 38 mm inner diameter and 280 mm length was used as the anode. The cathode was an SS wire of 0.5 mm diameter. Except for the electrodes, the vessel of the reactor was made of acrylic resin and the cathode was sustained by a ceramic insulator at the top and by Teflon threads at the bottom. A dc voltage of -3 kV ~ -34 kV was applied to generate discharge current of 0.01 mA ~ 2 mA in the corona discharge reactor. Pressure inside the reactor was atmospheric.

To study the influences of oxygen (O_2) and water vapor (H_2O) on the removal efficiency, the concentration of O_2 was adjusted by mixing a standard O_2 gas with the inlet gas of the reactor. The concentration of H_2O was controlled by bubbling N_2 through distilled water in a temperature-controlled bath.

The concentration of $(CH_3)_3N$ was analyzed using gas chromatography (Shimadzu Corp, GC 14B) with a flame ionization detector (FID). The concentration of H_2O was measured by a dew point hygrometer (Yokogawa Electric Corporation, MODEL 2586). When unknown reaction by-products were detected on a gas chromatogram, a gas chromatography mass spectrometer (GCMS) (Shimadzu Corporation, MS-QP1000S) was used to identify the reaction by-products. A derivative spectrophotometer (Yanaco New Science Inc., UO-1) was used to detect the concentration of SO_2 and NH_3.

Confirmation of ozone effect

Ozone (O_3) can be produced by corona discharge in air. Since O_3 is reactive, the ozonation reaction can be used to eliminate malodorous gases. To confirm the role and estimate the effect of ozone, two reactors connected serially were used, as shown in Fig 2. N_2-O_2 mixture was supplied to the first reactor to produce O_3 by corona discharge. $(CH_3)_3N$ was next mixed with the outlet gas from the first reactor, and the mixed gas was introduced to the second reactor. No voltage was applied on the second reactor, so no corona discharge occurred, and the second reactor simply provided space for the reaction of ozone with $(CH_3)_3N$. Then the concentration of $(CH_3)_3N$ at its outlet was measured. The decrease in the outlet concentration of the second reactor gives the O_3 effect.

Two-reactor system to prevent reaction by-products

The system shown in Fig 3 was proposed because the reaction by-products on the concurrent removal of $(CH_3)_3N$ and SO_2 from N_2-O_2 in a single reactor was comparatively high. To remove $(CH_3)_3N$ with little by-products, reactor no 1 employed a low discharge current while reactor no 2 employed a high current to remove the remaining SO_2. In this experiment the concentrations of $(CH_3)_3N$, SO_2 and O_2 were 45 ppm, 81 ppm and 20% respectively. Total flow rate was 432 cc/min.

RESULTS AND DISCUSSION

Removal of $(CH_3)_3N$

To evaluate the removal of $(CH_3)_3N$ by the deposition-type reactor, the definition of removal efficiency, Ψ, used in this work is as follows.

$$\Psi = (C_{in} - C_{out}) / C_{in} \qquad (1)$$

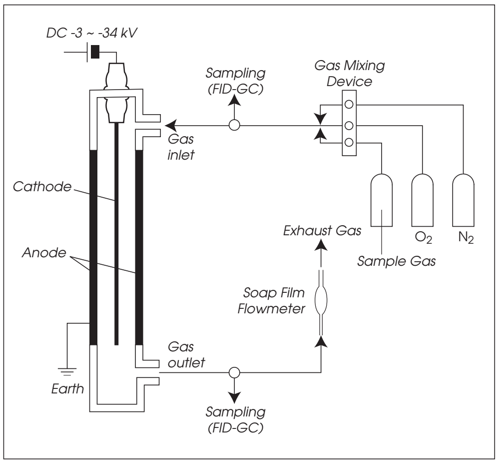

Fig 1. Schematic of experimental apparatus.

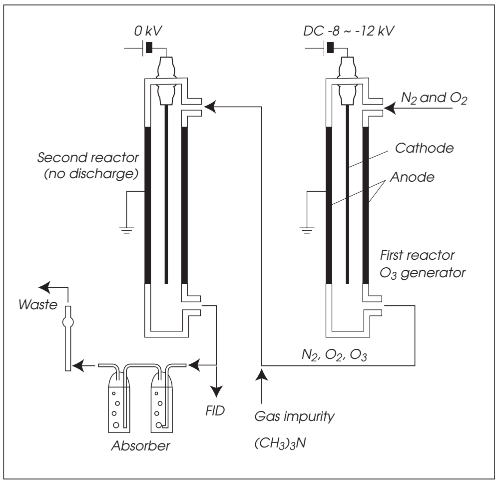

Fig 2. Apparatus to substantiate O_3.

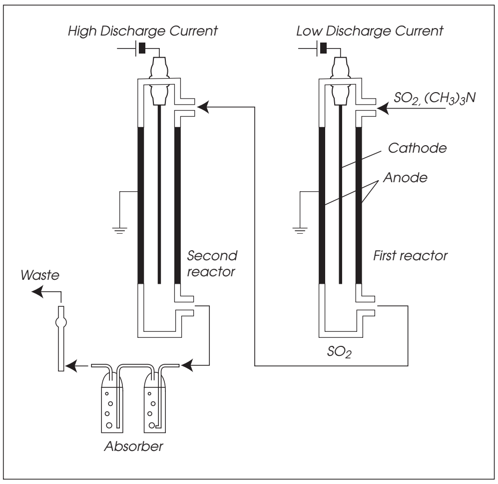

Fig 3. Removal of $(CH_3)_3N$ and SO_2 from N_2-O_2 using two-reactor system.

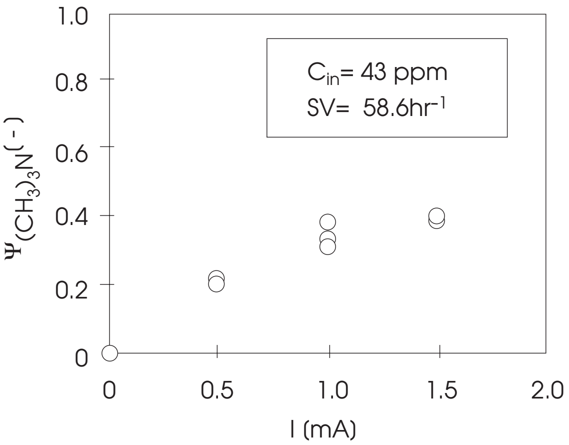

Fig 4. Removal efficiency of $(CH_3)_3N$ from N_2.

where C_{in} and C_{out} are, respectively, inlet and outlet concentrations of the pollutant in the gas sample.

Removal of $(CH_3)_3N$ from N_2

Fig 4 shows the removal efficiency of $(CH_3)_3N$ from N_2 against the discharge current, I. Obviously, though Ψ increased as the discharge current increased, it was difficult to achieve a complete removal. Identified by GCMS, at 1.5 mA discharge current the methane reaction by-product constituted about 7% of the inlet concentration of $(CH_3)_3N$ in terms of FID area.

Removal of $(CH_3)_3N$ from N_2-O_2 mixed gas and confirmation of ozone effect

Since the gaseous emission from a crematory furnace contains O_2 and H_2O, it is imperative to investigate the influence of O_2 and H_2O on the removal of gas impurities. Fig 5 shows the experimental results on the removal of $(CH_3)_3N$ from N_2-O_2. When the discharge current was as little as 0.15 mA, $(CH_3)_3N$ disappeared in the FID detection. Thus the presence of O_2 greatly enhanced Ψ.

To evaluate the effectiveness of electron attachment reaction, we calculated the average number of $(CH_3)_3N$ molecules removed per discharged electron. Called the electron efficiency, n_e, the ratio is given by Equation 2

$$n_e = N_r/N_{eo} \qquad (2)$$

Here N_r is the number of gas molecules removed per unit time, and N_{eo} is the number of electrons produced by the discharge current per unit time. On

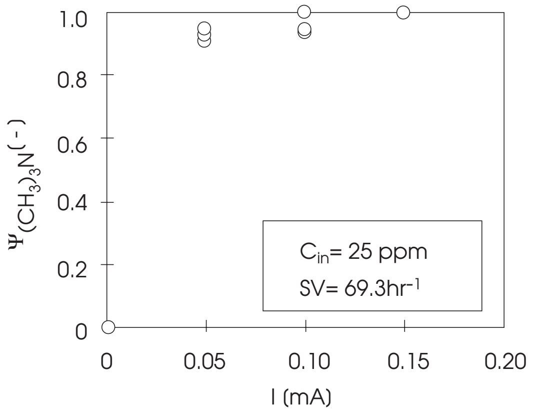

Fig 5. Removal efficiency of $(CH_3)_3N$ from N_2-O_2 mixed gas; C_{O_2} = 20%.

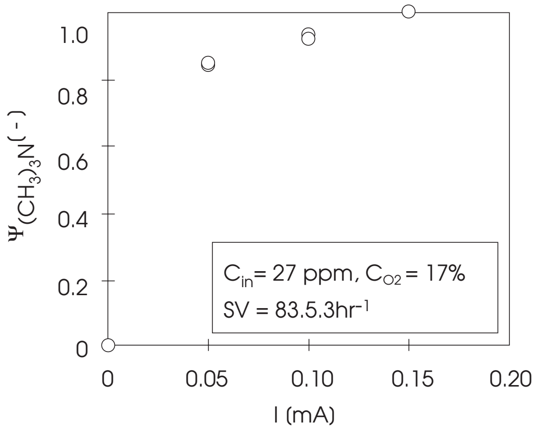

Fig 6. Effect of ozonation reaction on removal of $(CH_3)_3N$.

the removal of $(CH_3)_3N$, n_e was found to be 11.34 at the discharge current of 0.05 mA in the presence of 20% O_2. In other words, one electron contributed to the removal of about 11 molecules of $(CH_3)_3N$.

To explain such high removal efficiency, we should consider the role of ozone (O_3). As shown in Fig 2, N_2-O_2 mixture was supplied to the first reactor to produce O_3 by corona discharge. Then $(CH_3)_3N$ was mixed with the outlet gas from the first reactor. No voltage was applied to the second reactor, which only provided space for the ozonation reaction. It was also confirmed that, when O_2 was not present, no O_3 was detected at the outlet of the first reactor. Fig 6 shows the removal efficiency of $(CH_3)_3N$ due to the ozonation reaction. This independent experiment proves that the enhanced removal of $(CH_3)_3N$ can be attributed to the ozonation reaction, which generated reaction by-products. The by-products were identified by GCMS and listed in Table 1. As expected, the reaction by-products increased with the discharge current.

The generation of ozone by corona discharge takes place as a chain reaction system.[8,9]

$$O_2 + e \rightarrow O^- + O \qquad (3)$$

$$O + O_2 \rightarrow O_3 \qquad (4)$$

$$O^- + O_2 \rightarrow O_3 + e \qquad (5)$$

$$O_2 + e \rightarrow O + O + e \qquad (6)$$

$$O + O_2 \rightarrow O_3 \qquad (7)$$

As an example, at the discharge current of 0.05 mA, the generated concentration of ozone is approxiamtely 60 ppm, which is considerably higher than the inlet value of $(CH_3)_3N$ (28 ppm).

Removal of $(CH_3)_3N$ from N_2-H_2O mixed gas

Fig 7 shows the influence of H_2O on the removal of $(CH_3)_3N$ from N_2. A sufficiently high concentration of H_2O, C_{H_2O}, raised the removal efficiency, Ψ. Formation of reaction by-product was negligible.

Removal of NH_3

Removal of NH_3 from inert gas

Fig 8 shows the removal efficiency of NH_3 from inert gas (N_2 and He gas). The concentration of NH_3 was measured by the spectrophotometer. Obviously, it was difficult to achieve complete removal. Since NH_3 is weakly electronegative, only a small portion of electrons manage to attach to NH_3 molecules, thus resulting in a low removal efficiency. At 1.0 mA discharge current, some of the previously deposited NH_3 may have detached from the anode surface.

Removal of NH_3 from N_2-O_2 mixed gas

Fig 9 shows the removal efficiency of NH_3 from N_2-O_2 (20% O_2) against the discharge current. When the discharge current was increased to 0.4 mA, NH_3 was no longer detected with the spectrophotometer. This experiment exhibited high removal efficiency, as on the average 6.3 NH_3 molecules were removed by one electron.

Similar to the case of $(CH_3)_3N$, two reaction by-products with mass number of 44 and 59 were detected with GCMS but they have not been identified yet. Anyway it may be concluded that ozone must also have played a major role.

Influence of H_2O on removal of NH_3 from N_2-O_2 mixture (20% O_2)

Fig 10 shows the removal efficiency, Ψ_{NH_3}, against the discharge current, I, at three different concentrations of H_2O, C_{H_2O}. At discharge currents above 0.2 mA, the retardation effect of H_2O on Ψ_{NH_3} was quite clear. At very low discharge current (0.05 mA), H_2O appeared

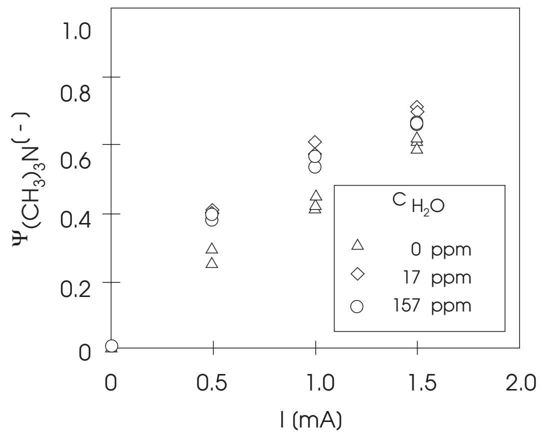

Fig 7. Influence of H_2O on removal of $(CH_3)_3N$ from N_2; $C_{(CH_3)_3N}$ = 81 ppm, SV = 75.9 hr^{-1}.

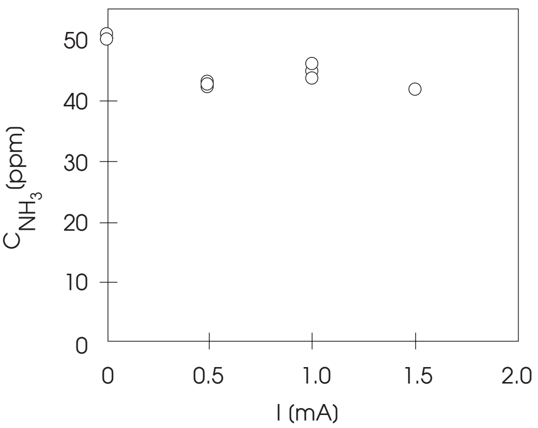

Fig 8. Removal of NH_3 from inert gas (N_2-He mixed gas) ; C_{NH_3} = 49 ppm, SV = 188.5 hr^{-1}.

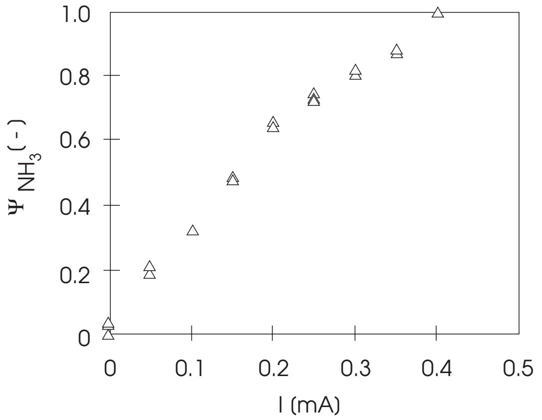

Fig 9. Removal of NH_3 from N_2-O_2 mixed gas; C_{NH_3} = 96 ppm, C_{O_2} = 20%, SV = 75.9 hr^{-1}.

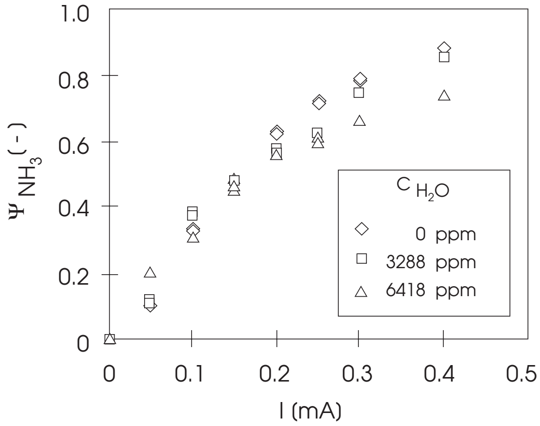

Fig 10. Influence of H_2O on removal of NH_3 from N_2-O_2; C_{NH_3} = 143 ppm, C_{O_2} = 20%, SV = 75.6 hr^{-1}.

to have some slight beneficial effect on Ψ_{NH_3}.

Since NH_3 is less electronegative than H_2O while O_2 is most electronegative, at low discharge currents the small number of electrons were mostly available for O_2 to produce O_3 and NH_3 was removed via ozonation reaction. At high discharge currents, there was an excess of electrons that can attach to H_2O. It is postulated that they then interfered with the formation of ozone and/or its reaction with NH_3. As a result, the NH_3 removal efficiency was slightly impeded at discharge currents above 0.2 mA.

Influence of SO_2 on removal of $(CH_3)_3N$

Firewood, oil and LP gas are all used to fire crematory furnaces in Thailand. When a low-grade oil is used, the exhaust gas will contain sulfur dioxide (SO_2). Therefore, it is important to investigate its effect on the removal of malodorous gases. Fig 11 shows the removal of $(CH_3)_3N$ from N_2-O_2 with co-existing SO_2. As seen from the Figure, when the discharge current became as little as 0.01 mA, the outlet concentration of $(CH_3)_3N$ disappeared at all three concentrations of SO_2. In fact, even without any discharge current the outlet concentration of $(CH_3)_3N$ became significantly lower than its inlet value because of a spontaneous reaction between $(CH_3)_3N$ and SO_2. Simply increasing the concentration of SO_2 led to a further decrease in the concentration of $(CH_3)_3N$ at zero discharge current. Also observed were white particles attaching on the inner surface of the reactor, the product of reaction between $(CH_3)_3N$ and SO_2. Nevertheless, it is interesting to investigate the concurrent removal of SO_2.

Fig 12 shows the change of SO_2 concentration with discharge current during the removal of $(CH_3)_3N$ from N_2-O_2 mixed gas. Obviously, the outlet concentration of SO_2 also decreased but it was difficult to remove SO_2 at low discharge currents.

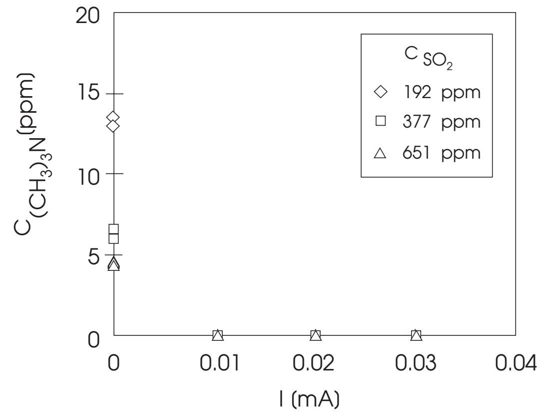

Fig 11. Decrement of $(CH_3)_3N$ on removal of SO_2 and $(CH_3)_3N$ from N_2-O_2 ; $C_{(CH_3)_3N}$ = 34 ppm, C_{O_2} = 17% and SV = 80.9 hr^{-1}.

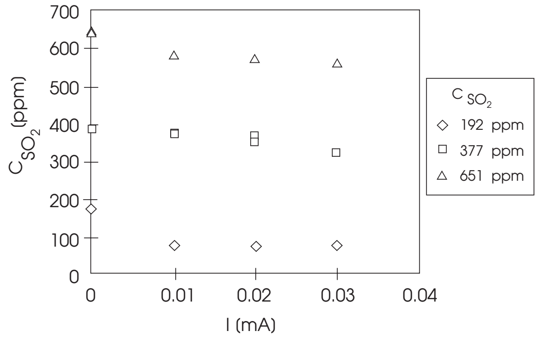

Fig 12. Concentration of SO_2 on removal of $(CH_3)_3N$ from N_2-O_2 ; $C_{(CH_3)_3N}$ = 34 ppm, C_{O_2} = 17% and SV = 80.9 hr^{-1}.

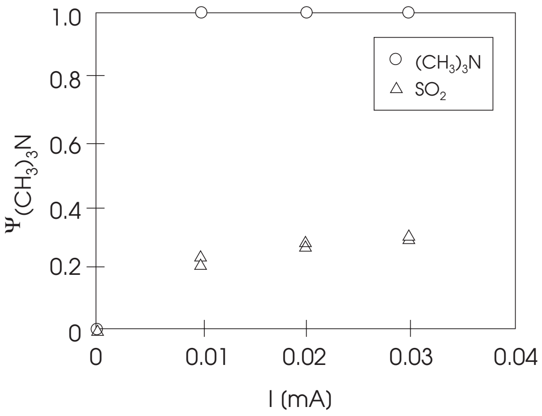

Fig 13. Removal of $(CH_3)_3N$ from N_2-O_2 in the first reactor ; C_{O_2} = 19%, $C_{(CH_3)_3N}$ = 45 ppm, C_{SO_2} = 81 ppm, SV = 81.6 hr^{-1}.

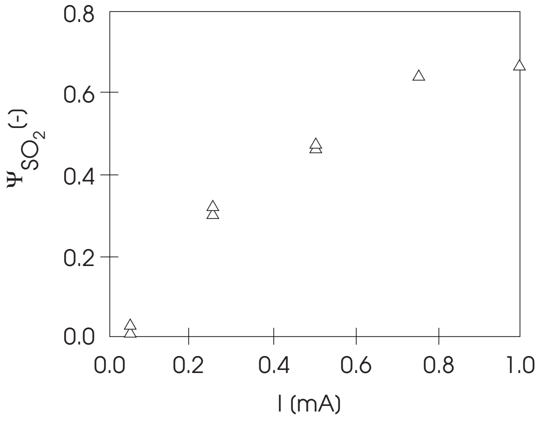

Fig 14. Removal of SO_2 in the second reactor ; C_{O_2} = 19%, $C_{(CH_3)_3N}$ = 0 ppm, C_{SO_2} = 81 ppm, SV = 81.6 hr^{-1}.

Technique to reduce reaction by-products and improve concurrent removal efficiency of SO_2

In the previous experiment, electron attachment reaction was found to show good promise for removal of $(CH_3)_3N$ as well as SO_2. However, it was difficult to effectively remove SO_2 at a low discharge current while undesirable reaction by-products tended to increase with the discharge current. The two-reactor system shown in Fig 3 was used to enhance the removal of $(CH_3)_3N$ and SO_2 from N_2-O_2 mixture.

The idea was to remove mainly $(CH_3)_3N$ at relatively low discharge currents in the first reactor in order to minimize reaction by-products and then remove the remaining SO_2 at higher discharge currents in the second reactor. The experimental results are shown in Fig 13. The generation of reaction by-products was negligible. By adopting the two-reactor system, essentially all $(CH_3)_3N$ can be removed in the first reactor and about 95% of the entire SO_2 can be removed with negligible generation of by-products.

CONCLUSION

Basic investigation into the individual removal of trimethylamine and ammonia from N_2 and air (N_2-O_2) has been carried out experimentally. In addition to the effect of water vapor, the influence and concurrent removal of SO_2 during the removal of $(CH_3)_3N$ have been elucidated. It may be said that the electron attachment reaction is effective for the individual removal of $(CH_3)_3N$ and NH_3 from air. More experimental work is underway on the removal of styrene and other malodorous gases in the crematory emission, particularly, the simultaneous removal of these gases. According to the present experimental results, a higher discharge current generally leads to a higher removal efficiency. The presence of O_2 in the gas mixture enhances the

Table 1. List of by-products generated on the removal of $(CH_3)_3$ N from N_2-O_2 mixture.

No	Retention Time (sec)	M/Z	M/Z of fragment	By-product	Amount at 0.05 mA	Amount at 0.1 mA
1	1.7	44	43, 42, 29, 28, 27	CH_3CHO	2%	5%
2	3.3	46	45, 44, 30, 31, 29	C_2H_5CH	4%	4%
3	4.9	58	57, 42, 29, 28, 27	$(CH_3)_2CO$	-	3%
4	6.9	61	60, 46, 45, 30, 29	CH_3NO_2	17%	19%

* The amount of by-product 19% means that, when the FID area of inlet concentration of $(CH_3)_3N$ is 100, the area of by-products generated is about 19.

removal efficiency of $(CH_3)_3N$ and NH_3 *via* ozonation reaction. On the other hand, the presence of water vapor enhances the removal efficiency of trimethylamine but retards that of ammonia.

Since reaction by-products are produced on the removal of $(CH_3)_3N$ from air in the presence of SO_2, a two-reactor system has been shown to remove both gases with negligible reaction by-products by independently adjusting the discharge current in each reactor. In short, the electron attachment reactor shows good promise for treating crematory and similar industrial emissions.

ACKNOWLEDGEMENTS

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NOMENCLATURE

C	=	concentration	[ppm]
Ψ	=	removal efficiency	[-]
I	=	discharge current	[mA]
SV	=	space velocity	[hr^{-1}]
V	=	discharge voltage	[V]
GC	=	FID area of gas chromatograph	[-]

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