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Hollow fiber membrane probes for the in situ spectrometric monitoring of nitrogen trichloride formation during wastewater treatment

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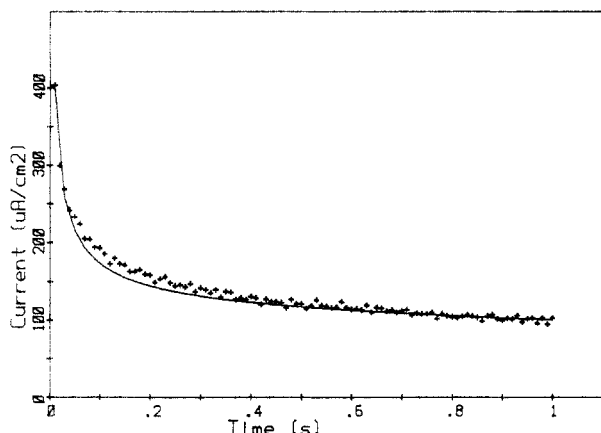


Figure 3. Potential step data (+) obtained after background subtraction when the potential of a 15% (w/w) graphite electrode was stepped from +0.6 V to -0.2 V vs Ag/AgCl (4.0 M KCl). The data shown is the average of four experiments on a single electrode with no polishing between runs. The solution contained 2 mM ferricyanide (1.0 M KCl, pH 2.8). Data collection was initiated at 10 ms after the step, with a total of 100 current measurements being made at 10-ms intervals. The solid line is the theoretical fit to the data.

is measured to ensure that it is below 100 Ω .

Chronoamperometric experiments have been used to characterize Kelgraf electrodes. In these experiments, the active surface area and the size of the active sites on the surface have been determined by fitting existing theory for microelectrode arrays to the experimental data. Weisshaar and Tallman (8) used this approach with the theory developed by Gueshi et al. (15). However, only after modification of the theory to include a distribution of two sizes of active sites were satisfactory results obtained. It was concluded that although the information obtained is useful, the model used to develop the theory is oversimplified with respect to the actual distribution and size of sites on the Kelgraf electrode surface. We have performed similar experiments with electrodes fabricated as described above. However, the theory of Shoup and Szabo (16) was used in the simplex optimization for the determination of the active area and site radii. This theoretical expression for the current has been shown to be more accurate than that used previously although it uses the same model for the distribution of active sites on the surface. Figure 3 shows the experimental potential step data obtained for the reduction of 2 mM ferricyanide at a 15% (w/w) graphite electrode after background subtraction. The experimental conditions are given in the caption. Also shown in Figure 3 is the theoretical fit (solid line), which is much better than that obtained in the study mentioned above when only one size of active site was considered. For one 15% (w/w) graphite electrode used in this study, the surface was found to be 18.0% active with a standard deviation of 0.15%. The active site radii determined were 25.0 μm (standard deviation 1.5). These

results are from four sets of experiments as described in the caption to Figure 3, with polishing between sets. This active site radius is in agreement with values determined previously by using chronoamperometry and scanning electron microscopy (8). In terms of reproducibility, results from another 15% electrode fabricated by a different individual yielded a percent active area and site radii of 21% and 30 μm , respectively. This variation between electrodes undoubtedly results from differences in the mixture preparation rather than from the compression molding step. It is this later step that we have attempted to refine, and its reproducibility is excellent with respect to the success rate and physical characteristics of the product. There are various reasons why our theoretical fit appears to be better than the results reported previously. Obviously the theory used was different. In addition, the fabrication technique is somewhat different as is the particle size of the graphite used to prepare the electrodes. Even though our results are rewarding, we agree with the previous conclusions that the model used to derive the theory is undoubtedly much simpler than the conditions that exist at the electrode surface. However, the percent active area and active site radii determined here are still useful in that they are important in determining the enhancement effects associated with microelectrode arrays in stationary solutions and flowing streams (17).

LITERATURE CITED

- (1) Anderson, J. E.; Tallman, D. E.; Chesney, D. J.; Anderson, J. L. *Anal. Chem.* **1978**, *50*, 1051-1056.
- (2) Anderson, J. E. Ph.D. Dissertation, North Dakota State University, 1979.
- (3) Chesney, D. J.; Anderson, J. L.; Weisshaar, D. E.; Tallman, D. E. *Anal. Chem.* **1981**, *53*, 321-331.
- (4) Weisshaar, D. E.; Tallman, D. E.; Anderson, J. L. *Anal. Chem.* **1981**, *53*, 1809-1813.
- (5) Tallman, D. E.; Weisshaar, D. E. *J. Liq. Chromatogr.* **1983**, *6*, 2157-2172.
- (6) Anderson, J. L.; Whiten, K. K.; Brewster, J. D.; Ou, T. Y.; Nonidez, W. K. *Anal. Chem.* **1985**, *57*, 1366-1373.
- (7) Cox, J. A.; Kulkarni, K. R. *Talanta* **1986**, *33*, 911-913.
- (8) Weisshaar, D. E.; Tallman, D. E. *Anal. Chem.* **1983**, *55*, 1146-1151.
- (9) Petersen, S. L.; Weisshaar, D. E.; Tallman, D. E.; Schulze, R. K.; Evans, J. F.; DesJarlais, S. E.; Engstrom, R. C. *Anal. Chem.* **1988**, *60*, 2385-2392.
- (10) Commercial Chemicals Division 3M, Technical Information, Y-ICKM (28.1) R1.
- (11) Petersen, S. L.; Tallman, D. E. *Anal. Chem.* **1988**, *60*, 82-86.
- (12) Klatt, L. N.; Connell, D. R.; Adams, R. E.; Honigberg, I. L.; Price, J. C. *Anal. Chem.* **1975**, *47*, 2470-2472.
- (13) Shah, M. H.; Honigberg, I. L. *Anal. Lett.* **1983**, *16*(A15), 1149-1163.
- (14) Anderson, J. E. *Am. Lab. News* **1988**, December, 54, 55.
- (15) Gueshi, T.; Tokuda, K.; Matsuda, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *89*, 247-260.
- (16) Shoup, D.; Szabo, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *160*, 19-26.
- (17) Cope, D. K.; Tallman, D. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *205*, 101-123.

RECEIVED for review May 9, 1989. Accepted July 18, 1989. The authors acknowledge financial support of this work by the Committee for Institutional Studies and Research at Murray State University.

Hollow Fiber Membrane Probes for the In Situ Mass Spectrometric Monitoring of Nitrogen Trichloride Formation during Wastewater Treatment

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The utility of mass spectrometry in the broad field of process analytical chemistry and in situ analysis has grown steadily over the past few years (1, 2) with concurrent re-

finements in mass spectrometers and their inlet systems. In our case, these mass spectrometers are used for a variety of analyses (3, 4). The characteristic role is to apply its excellent

sensitivity, good selectivity, and real time data capabilities. The challenge, in diverse applications, is the development of appropriate interfaces and inlet systems. They must be rugged, reliable, sensitive, and applicable to a wide range of sample environments.

This communication deals with the utility of a hollow fiber membrane interface developed several years ago in our laboratory (5) and since modified for this application. Other researchers have discovered its utility and have found numerous applications (6-9). However, some chemical processes in an industrial setting test the limits of any sampling technology. High temperatures, low or high pressures, corrosive or caustic environments, and rapidly changing dynamic processes, along with the sheer size of some of the processes, make for interesting research.

We have examined the utility of a hollow fiber membrane probe interface in the monitoring of potential NCl_3 (nitrogen trichloride) formation during bleach chlorinolysis treatment of chemical waste streams containing ammonia or other nitrogen-containing species. NCl_3 is an explosively unstable compound that will detonate above its boiling point of 71 °C, when catalyzed by light, and at concentrations above about 2000 ppm (10, 11).

Real-time monitoring of the process is necessitated by the transient stability of NCl_3 . Common trap and off-line analysis methods would prove difficult to use and since we do not know when to expect any formation to occur, we need to monitor the process during all of its stages. Off-line methods would only be able to provide time-averaged data, perhaps across several significant events. Self-evident safety factors also exist. In general, the unstable nature of NCl_3 necessitates a sensitive, real time monitoring method.

While this communication will discuss the application of mass spectrometry to chlorinolysis waste treatment, the intent is to demonstrate the general utility of a silicone hollow fiber membrane probe with in situ mass spectrometry, rather than specifying reaction conditions for successful wastewater treatment.

EXPERIMENTAL SECTION

In Situ Mass Spectrometer. The mass spectrometer is an in-house built unit based on a Balzers QMG-511 quadrupole mass spectrometer. The mass scanning range of the instrument is 1-1023 amu. An off axis 17-stage discrete dynode electron multiplier is used for ion detection after ion energy filtering through a 90° electrostatic sector. A Balzers gastight ion source was used for this work.

The quadrupole mass spectrometer vacuum housing is evacuated by a 270 L/s Balzers turbopump backed by a 310 L/min Alcatel direct drive pump, which is also used for system roughing. All of the MS control electronics, vacuum systems and auxiliary electronics are housed in a cabinet that can be purged with inert gas for hazardous area work. An explosion-proof roughing pump is located outside of the cabinet and cooling is provided by an external Neslab CFT-75 recirculating coolant refrigerator system (Portsmouth, NH). Cooling of the cabinet is necessary due to heat buildup by the electronics and turbopump.

The QMG-511 mass spectrometer is operated either by manual means or by computer. The data system is a DEC PDP 11/23 based system using two RL01 disk drives. In-house-written software was used to control all functions of the mass spectrometer. I/O between the computer and mass spectrometer occurred through a parallel communications cable which may be up to 300 m in length. In this study, due to the explosion potential of the experiment, the computer and operator were stationed in an office area about 15 m away from the mass spectrometer and chemical reactor. The separate coolant refrigerator was placed near the mass spectrometer. The mass spectrometer itself was positioned just outside the lab hood which houses the chemical reactor.

Chemical Reactor. The chlorinolysis experiments were performed with a bench scale reactor inside a flow hood. A 1-L round-bottomed flask reactor was equipped with a side arm

take-off, mechanical stirrer, reflux condenser, thermometer, combination pH electrode, and feed ports for adding waste feed, 10% NaOCl bleach solution, 15% NaOH, and 15% HCl. The acid and base provide pH control as needed. The pH was measured by the combination electrode and an automatic control circuit measured the caustic and acid into the reactor with calibrated FMI fluid metering pumps. An infrared heating lamp and temperature regulator circuit were also utilized to achieve temperature control.

Two modes of operations were studied, batch versus continuous chlorination. In the batch run, 350 mL of organic waste adjusted to pH 7 was heated to 100 °C. The pH control was started and adjusted to typically pH 5.5. The automatic pH controller maintains this value throughout the run. Normal operation involves the addition of caustic, as HCl was evolved during the process. At this point the bleach flow was started and added as fast as possible without venting any chlorine. Grab samples were taken at regular intervals to determine the chlorine concentration in solution by iodimetric titration. The bleach flow rate was adjusted accordingly to maintain a constant amount of chlorine, typically 1000 ppm, in solution. The reaction reached its end point when the chlorine concentration was seen to rise.

In the continuous mode of operation waste and bleach are added continuously. The feed rates are adjusted to allow several reactor turnovers before allowing the contents to flow out through a side port. Batch operations are usually preferred for small scale processes where not enough waste is being generated to sustain a continuous mode of operation.

Hollow Fiber Probe. Sampling of the chemical process occurred at two points. One monitor was set at the vent of the reflux condenser and the second was placed directly inside the reactor headspace. The reactor environment is 100 °C water saturated with high concentrations of Cl_2 and HCl gases along with CO_2 , chlorinated organics, and other byproducts of the chlorinolysis reaction. Due to the harsh operating conditions present during the reaction, research was performed to find a suitable sample inlet system, detailed below.

The species of prime interest was any detectable NCl_3 being formed. NCl_3 concentrations of a few thousand parts per million are explosive. To guarantee a suitable safety margin, our detection limit must be much lower. To ensure proper operation of the mass spectrometer, the large background from water vapor must be eliminated and high vacuum maintained.

A molecular leak probe, consisting of a quartz tube collapsed to a fine 10- μm hole size, was tried for sampling. However, too much water was let into the instrument vacuum system which raises the operating pressure and water background unacceptably high. The molecular leak probe suffered also from condensation of liquids on the probe tip. Drops formed or splashed there during reaction monitoring plugged the micrometer orifice and gave unstable signals.

With hollow fiber probes, factors such as the membrane material's area, thickness, and temperature can often be varied to find suitable characteristics. A non-cross-linked silicon polymer hollow fiber (Dow Corning non-cross-linked silicon medical tubing 0.008 in. o.d., 0.007 in. i.d.) has been found in the past (5) to provide fast response and excellent separation of organics from water. A sample probe was devised from this material. The open ends of two 3 cm lengths of tubing were looped and sealed into the end of a 1/4 in. o.d. Pyrex tube with Dow Corning 721 RTV silastic adhesive. The opposite end of the Pyrex tube was connected to the mass spectrometer ion source vacuum system via 1/4 in. o.d. Teflon tubing. In this manner the inside of the hollow fibers is held under vacuum while the exterior is exposed to the sample environment. Volatile organics soluble in the fiber materials pass through the probe and into the mass spectrometer ion source. Air and water, being generally less soluble in the polymer material, are thereby greatly excluded (5).

The non-cross-linked silicone polymer hollow fiber probe was initially evaluated by sampling air over an Erlenmeyer flask of boiling water. This would test the vacuum attainable as well as the stability of the probe which to date had only been used to sample systems up to 60 °C (12, 13). Vacuum system pressures from the non-cross-linked silicone polymer probe were totally unacceptable at temperatures higher than 75 °C. At 100 °C the probe material swells open to the point that pumping directly

Table I. Positive Ion Electron Impact Mass Spectrum of NCl_3

m/e	rel abund	ion species
49	54	N^{36}Cl^+
51	18	N^{37}Cl^+
84	100	$\text{N}^{36}\text{Cl}_2^+$
86	65	$\text{N}^{36}\text{Cl}^{37}\text{Cl}^+$
88	10	$\text{N}^{37}\text{Cl}_2^+$
119	5	$\text{N}^{36}\text{Cl}_3^+$
121	5	$\text{N}^{36}\text{Cl}^{37}\text{Cl}_2^+$

on the probe with a 195 L/min Alcatel vacuum pump could not keep the pressure below 100 Torr (uncorrected). Additionally the swelled hollow fibers were found to be easily broken; mild shocks tended to tear open the fiber material, venting the vacuum system. This system would be unlikely to survive any bumping, splattering, or explosions of NCl_3 potentially expected in this study.

Several different designs of supported hollow fiber probes were evaluated. The non-cross-linked material was dissolved in toluene and applied to a variety of frit glass and stainless steel screen probe designs. Although these systems did prove more physical stability to the probe, the problem of poor vacuum still existed. A much thicker material probe was considered, but rejected based on the conclusion that response times would be too slow compared to the real time needs of monitoring for an explosive material.

A cross-linked silicone polymer hollow fiber (Dow Corning Silastic medical grade tubing 0.02 in. i.d., 0.025 in. o.d.) was tried next in the above described loop design. Cross-linking is done by the manufacturer to add strength to the material. The cross-linked material response time was found in the past to be longer and, therefore, less desirable than for the non-cross-linked material (5, 14). But, a cross-linked silicone polymer probe was found to perform well in the water vapor test. Vacuum pressure at 100 °C over boiling water was about 10 μm (uncorrected) for a single loop design. This was very close to the absolute pressure attainable with this pump. The material was also seen to be physically tougher, able to resist knocks without tearing. To test stability to an acidic environment, the probe was exposed to concentrated vapors of HCl just inside the neck of an open bottle of HCl acid for 30 min. These experiments produced no noticeable effect on the probe. The RTV silastic adhesive used to seal the fiber into the probe body showed excellent sealing and stability properties under both of these tests and after a few days of curing, a negligible background. A double loop probe of the above design was built for insertion into the reaction vessel. A second probe was fashioned to sample the relatively low concentration sample region at the vent of the reflux condenser. At this point the headspace vapor should be near ambient temperature and most of the organic vapors condensed out. A non-cross-linked fiber was used here for its fast response and greater sensitivity. The probe was of similar design to the above concept. One end of five hollow fibers was set with adhesive into a $1/4$ in. stainless steel tube. The free ends were sealed with a dab of adhesive. Either probe could be sampled by a system of valves and a pump that kept the unsampled probe under vacuum.

DISCUSSION

Table I lists the mass spectrum of nitrogen trichloride obtained from an internal source. Since no provision is made for chromatographic separation of the various chemical species, we must choose characteristic ions to monitor. m/z 84 (NCl_2^+) is the base peak in the mass spectrum and is the logical choice for sensitive real time monitoring. However, it suffers from several direct mass interferences from chlorinated hydrocarbon fragments we would expect to see in the chlorinolysis of organic wastes (CH_2Cl_2^+ , $\text{C}^{36}\text{Cl}^{37}\text{Cl}^+$, etc). Lower mass fragments were considered but rejected due to the increased problems of interferences. The NCl_3 parent ions at m/z 119 and 121, though at weaker intensity than the base peak, could provide a unique pattern for identification. Most simple chlorinated hydrocarbon species would give a strong m/z 117 ion while NCl_3 would not. Thus the presence of m/z 84 and 119 peaks

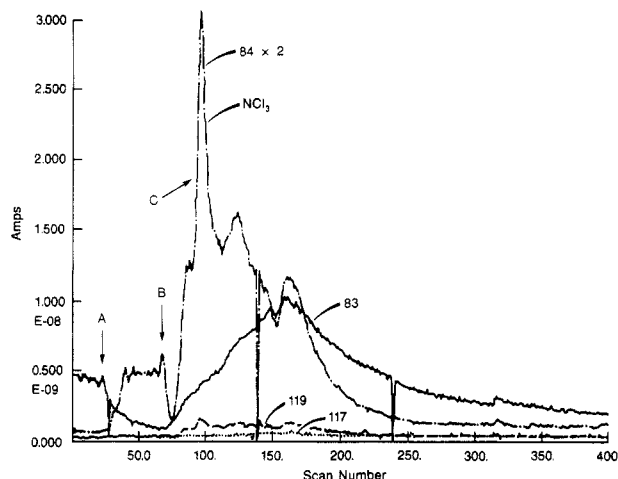


Figure 1. Selected ion plot for bleach reaction with 0.1% ammonia solution: (A) start of bleach flow; (B) end of oxidation reaction; (C) NCl_3 surge.

without corresponding increase of m/z 117 was used as a criterion for the presence of NCl_3 .

Those ions were monitored during the analysis, but to provide full information in case the spectra were complicated, the mass spectra were scanned from 10 to 300 amu. The data system allowed us to scan the low mass part of the spectrum, 10–75 amu, at low sensitivity and the 75–300 amu range at high sensitivity by changing the multiplier voltage in between.

Preliminary experiments, accomplished by injecting small amounts of chlorinated organics into the reactor vessel, showed system response time to be about 5–10 s and with part per million sensitivities. We saw no reason to pursue sensitivity studies with NCl_3 , lacking a new standard, and since the explosive concentration is reportedly a few percent in air. Relative sensitivity for NCl_3 is expected to be equivalent to similar chlorinated hydrocarbons.

The reactions of dilute aqueous solutions of chlorine and ammonia are very complex but have been studied extensively (15–17). In order to better understand the conditions under which NCl_3 might be formed under chlorinolysis of organic wastes in our system, several model experiments were performed using 0.5% ammonia solutions (from NH_4Cl) in water. A 350-mL aliquot of ammonia solution, in the previously described batch mode system, was substituted at pH 5.5 and 100 °C before the start of the mass spectral data accumulation. Figure 1 shows a selected ion plot of the reaction sequence obtained from the reaction flask probe. m/z 84 is plotted at 2 \times normal intensity to more clearly show its behavior above the other plotted ions. NCl_3 forms and degrades very rapidly in the headspace. At a molar ratio of bleach/ NH_3 equal to about 3, a surge of NCl_3 is seen. From the figure the m/z 84 and 119 peaks are seen to surge at point C while the m/z 117 peak remains flat. By the above criteria, this indicates the presence of NCl_3 .

Figure 2 shows a typical mass spectrum at the greatest yield of NCl_3 . The spectrum shows a good match for the earlier standard spectrum. The small, higher-mass peaks are identified to be from the decomposition of the exposed 1 cm^2 surface of a rubber stopper used to hold the pH probe. The stopper was only exposed to the headspace vapors but was severely corroded and was replaced by a glass feed-through in later experiments. This gives a feel for the severe conditions in the reactor.

Another series of trial runs was performed in which the reactor was run in a continuous feed mode. The 0.5% ammonia solution, used to represent a waste stream, was continuously fed into the reactor along with the bleach solution. The reactor was initially loaded with waste and adjusted to

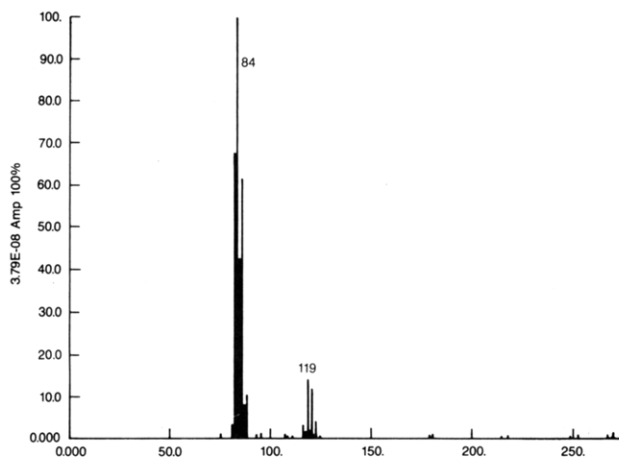


Figure 2. Mass spectrum of NCl_3 above m/z 75.

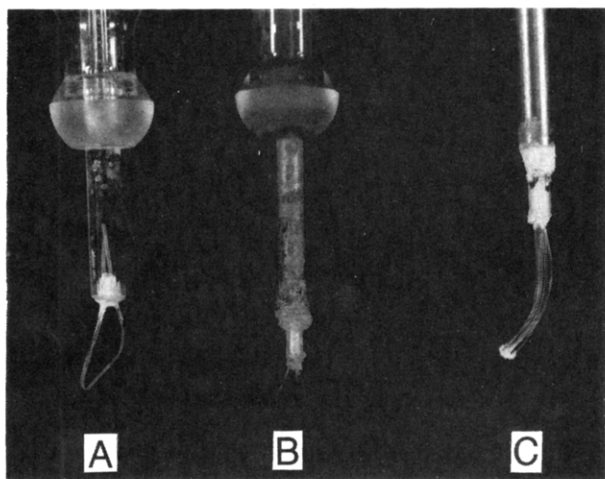


Figure 3. Photograph of probes used in chlorinolysis reaction: (A) Cross-linked probe from reactor headspace; (B) non-cross-linked probe from reactor vent exposure to reactor system; (C) non-cross-linked probe for comparison to B above.

pH 5.5 and 100 °C. The waste and bleach solutions were started simultaneously. Product was allowed to escape through the side arm of the reactor. Feed and exhaust rates were adjusted to ensure several reactor turnovers to occur. The chlorine concentration in solution was determined by periodic grab samples and the bleach flow was adjusted to keep the concentration at 1000 ppm. For this test the run continued at pH 5.5 for 2 h and was lowered to pH 4 for 20 min with a $[\text{Cl}_2] = 800$ ppm then to pH 2.0–2.5 $[\text{Cl}_2] = 100$ ppm for 30 min. The pH was then raised to pH 6 for 60 min $[\text{Cl}_2] = 1000$ ppm and then shut down. In situ monitoring of the entire sequence showed no build up of NCl_3 such as had been seen in the batch mode of operation. Since the solubility of chlorine in water is very low at a pH less than 4, the reactor headspace and vent were exposed to high concentrations of chlorine gas for an extended period of time. The cross-linked hollow fiber probe worked admirably under these conditions, and at the end of the experiment showed no signs of deterioration. The non-cross-linked probe above the condenser vent suffered traumatic failure however. Figure 3 is a photograph of the probes used in this experiment. Probe A with a body of Pyrex glass was the one used in the reactor headspace. No signs of deterioration were apparent, even after this work and dozens of more hours of testing. Probe B with a 316 stainless steel body was the one from the reactor vent after the above reaction sequence. For comparison a similar design probe, of the same material and makeup, though with a glass shaft, is shown as C. The non-cross-linked material had become stiff and fragile and indeed had snapped off upon removal from

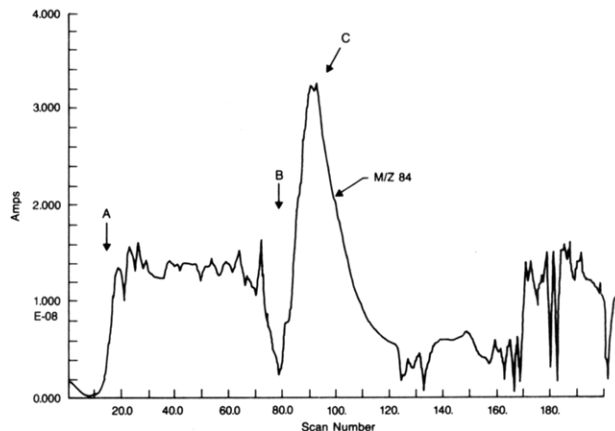


Figure 4. Selected ion plot chlorinolysis reaction: (A) start of bleach flow; (B) end of oxidation reaction; (C) NCl_3 buildup.

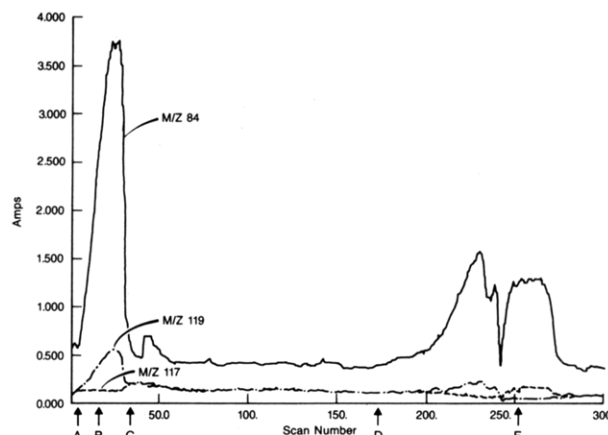


Figure 5. Selected ion plot of temperature upset during continuous bleach chlorinolysis: (A) heating lamp failure; (B) brine feed off; (C) heating lamp fixed, feed back on; (D) heating lamp turned off; (E) heating lamp turned back on.

the reactor. The RTV Silastic both in the vent and headspace showed good stability. The type 316 stainless steel body and the probe shows marked deteriorations too. Further probe bodies were made of glass.

Experiments were next performed that used synthetic waste samples containing 500–1000 ppm total organic carbon (TOC), mostly nitrogen-containing species. In a batch mode operation, Figure 4, similar to the experiment using an ammonia solution, a surge of NCl_3 is seen at a point when the oxidation reaction is essentially complete and the chlorine is building up in solution. Similarly, a test of the reactor in the continuous mode at pH values ranging from 2.0 to 10 showed no NCl_3 formation. The specific ion–time curve is essentially similar to the above model experiment.

A final experiment was performed to test the importance of the reactor temperature control and shows the utility of in situ monitoring. Figure 5 shows a specific ion–time curve from an intermediate time in a continuous chlorinolysis reaction where the heating lamp was shut off to allow the temperature to drop to 85–90 °C. At around this point is seen a large upsurge of NCl_3 in the headspace. The reactor feed immediately was shut down and the lamp turned back on for fear of an explosion, though none occurred. After reequilibration of the system, the experiment was duplicated a few minutes later as shown in the figure. Again the NCl_3 concentration was seen to rise with a decrease in temperature and to fall when temperature equilibrium was again established. It is suggested that the phenomenon occurs due to a complex change in the solubilities of key intermediates in the NCl_3 formation. These complexities were forecast, thus necessitating the need for in situ monitoring. Regardless of the

mechanism, it can be seen that the hollow fiber probe and in situ mass spectrometer can be successfully used to monitor these harsh reactor conditions for an explosive material with good long-term performance from the probe and mass spectrometer.

ACKNOWLEDGMENT

The work of Karl Krumel in this project is gratefully acknowledged.

Registry No. NCl_3 , 10025-85-1; water, 7732-18-5.

LITERATURE CITED

- (1) Collis, J. B.; Illman, D. L.; Kowalski, B. R. *Anal. Chem.* **1987**, *59*, 624A.
- (2) Meuzelaar, H. L. C.; Windig, W.; Huff, S. M.; Richards, J. M. *Anal. Chim. Acta* **1986**, *190*, 119.
- (3) Kallos, G. J.; Tou, J. C. *Environ. Sci. Technol.* **1977**, *11*, 1101.
- (4) Tou, J. C.; Reddy, D. Presented at 35th ASMS Conference on Mass Spectrometry and Allied Topics, Denver, 1987; *Anal. Chim. Acta*, in press.
- (5) Westover, L. B.; Tou, J. C.; Mark, J. H. *Anal. Chem.* **1974**, *46*, 568.
- (6) Bler, M. E.; Cooks, R. G. *Anal. Chem.* **1987**, *59*, 597.
- (7) Hwang, H.; Dasgupta, P. K. *Anal. Chem.* **1987**, *59*, 1356.
- (8) Brodbelt, J. S.; Cooks, R. G. *Anal. Chem.* **1985**, *57*, 153.
- (9) Brodbelt, J. S.; Cooks, R. G.; Tou, J. C.; Kallos, G. J.; Dryzga, M. R. *Anal. Chem.* **1987**, *59*, 454.
- (10) *Dangerous Properties of Industrial Materials*; Sax, N. I., Ed.; Van Nostrand Reinhold: New York, 1984.
- (11) Schlesinger, G. G. *Chem. Eng. News* **1966**, *44*, 46.
- (12) Tou, J. C.; Westover, L. B.; Sonnabend, L. F. *J. Phys. Chem.* **1974**, *78*, 1096.
- (13) Tou, J. C.; Westover, L. B.; Sonnabend, L. F. *Am. Ind. Hyg. Assoc. J.* **1975**, 374.
- (14) Crummett, W. B.; Tou, J. C.; Cortes, H. J.; Fawcett, T. G.; Kallos, G. J.; Martin, S. J.; Putzig, C. L.; Turkelson, V. T.; Yurga, L.; Zakett, D. *Talanta* **1989**, *36*, 63.
- (15) Frazier, S. E.; Sesler, H. H. *Chloramination Reactions, Benchmark Papers in Inorganic Chemistry* 6; Dowden, Hutchinson and Ross, Inc.: PA, 1977.
- (16) White, G. C. *Handbook of Chlorination*; Van Nostrand Reinhold: New York, 1972.
- (17) Corbett, R. E.; Metcalf, W. S.; Soper, F. G. *J. Chem. Soc.* **1953**, 45, 1927.

RECEIVED for review March 16, 1989. Accepted July 19, 1989.