# Investigation of Approaches for the Determination of Inorganic Chloramines in Workplace Air

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16. Abstract (Limit: 200 words) Direct reading instrument methods for determining the concentration of inorganic chloramines in the air at work sites were investigated. Infrared spectrometry allowed the detection of gaseous nitrogen-trichloride (10025851) in atmospheres low in carbon-dioxide. Under comparable conditions it was not possible to identify either monochloramine (10599903) or dichloramine (51752). Under atmospheric levels of carbon-dioxide, the nitrogen-trichloride absorbance band was completely obscured by carbon-dioxide sidebands. Although detector tubes for chlorine reacted with nitrogen-trichloride, the presence of trace amounts of molecular chlorine interfered, making the use of detector tubes unworkable. Mass spectrometry with selected ion monitoring detected nitrogen-trichloride. Nitrogen-trichloride was stable in a glass/polytetrafluoroethylene sample bulb for over 48 hours. There were problems with the introduction of nitrogen-trichloride into the instrument. The presence of amines did not seriously affect the mass spectral intensities of nitrogen-trichloride. Even after a 4 hour period the introduction of primary amines did not appreciably change the mass spectral intensity. The author concludes that mass spectrometry appears to be the technique to use for the analysis of nitrogen-trichloride. A more easily managed method for sample introduction to the system was needed.

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## ABSTRACT

Several approaches for the determination of inorganic chloramines in workplace air were examined. Because of the limited stability of these compounds, the focus was on the use of direct reading instruments. Therefore, Fourier-transform infrared spectrometry (FT-IR), direct reading indicator tubes ("detector tubes"), and mass spectrometry were considered.

Gaseous nitrogen trichloride ($NCl_3$) could be detected by infrared spectrometry by its absorbance band at 650 $cm^{-1}$ in atmospheres low in carbon dioxide. However, monochloramine or dichloramine could not be detected under comparable conditions. When atmospheric levels of $CO_2$ were introduced, the sidebands of the 666 $cm^{-1}$ $CO_2$ absorbance band completely obscured the $NCl_3$ absorbance band. This indicated that an FT-IR approach was unfeasible.

The use of detector tubes also proved unworkable. Detector tubes for chlorine, which were based on o-tolidine, were found to react with $NCl_3$. The presence of trace amounts of molecular chlorine present under conditions favorable for $NCl_3$ formation eliminated the use of these detector tubes because of the non-specificity of, and the low levels of oxidizer needed for, the o-tolidine reaction. In an attempt to eliminate the molecular chlorine, a silver membrane prefilter was inserted in front of the detector tube. However, mass spectrometry confirmed that small amounts of molecular chlorine could pass through the silver membrane filter and interfere.

Nitrogen trichloride was detected by mass spectrometry using selected ion monitoring. Both the parent ion ($NCl_3^+$) and daughter ion ($NCl_2^+$) of $NCl_3$ could

be observed. $NCl_3$ was found to be stable in a glass/polytetra-fluoroethylene sample bulb for over 48 hours. Introduction of the $NCl_3$ into the instrument is problematic; the ion intensities for $NCl_3$ ions were extremely variable (up to 44% RSD). Nitrogen trichloride intensities were not seriously affected by the presence of amines. When samples of primary amines were introduced (as liquids), the mass spectral intensity did not appreciably change, even after 4 hours. Based on this research, mass spectrometry appears to be a promising technique for analysis of $NCl_3$, however, additional research is required to formulate a sample introduction approach that could yield quantitative information.

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## Introduction

Recent investigations have suggested links between chloramine exposure and respiratory problems in workers.[1-5] In an earlier investigation at a poultry processing plant, chloramines were suspected as the agent responsible for complaints of irritation by employees and field inspectors.[1] In a more recent case, an industrial hygienist investigating cases of hypersensitivity pneumonitis (HP) at a municipal swimming pool suggested a link between the outbreak of HP and chloramines.[2] Subsequently, the Colorado Department of Health requested that researchers at NIOSH develop a sampling and analytical method for the determination of chloramines in workplace atmospheres. Therefore, an investigation of the feasibility of a sampling and analytical method for chloramines was initiated.

The term "chloramine" does not apply to a single compound but rather to any of the chlorinated amines of the general form R'R"NCl, where "R" is either a chlorine, a hydrogen, an alkyl, or an aryl group. These could be roughly divided into the "inorganic" chloramines, which have only hydrogen and chlorine ($NH_2Cl$, $NHCl_2$, and $NCl_3$), and the "organic" chloramines. The properties of this diverse group of compounds vary considerably and thus a single method for all "chloramines" is not practical. Nitrogen trichloride ($NCl_3$) is the most volatile of the chloramines and is a suspected irritant. Further, $NCl_3$ and the other inorganic chloramines could be formed as part of operations in the workplaces noted above.

Information on the properties of the inorganic chloramines is scarce. The melting point of monochloramine ($NH_2Cl$) is -66 °C, and although its vapor pressure is appreciable, specific values are not available. Similarly, no information is available on dichloramine ($NHCl_2$), undoubtedly because the pure compound has not been isolated. More information is available on nitrogen

trichloride ($NCl_3$). $NCl_3$ is capable of being formed depending on the relative concentrations of ammonia, hypochlorite, and the pH. It is noted to be readily released from aqueous solutions upon aeration and is photosensitive.[6] Nitrogen trichloride can also be formed in the gas phase.[7] Its melting point is -40 °C, boiling point is 71 °C, and it has a vapor pressure of 150 mm Hg at 20 °C. No exposure limits (OSHA permissible exposure limit or NIOSH recommended exposure limit) exist for any of the chloramines.

Health Effects

Studies of the health effects of "chloramines" in solution generally have not differentiated which species were investigated or have dealt with a large class of organic chloramines.[8-11] While there have been no human exposure studies of the inorganic chloramines, owing to a lack of a monitoring method, exposure studies have been performed on animals dosed with monochloramine or $NCl_3$. In part, these early studies were prompted by the effects of "agenized" flour, i.e., flour treated with $NCl_3$. Nitrogen trichloride reacted with methionine in the flour to form a sulfoximine. The flour caused some animals to go into convulsive fits ("ataxia"), sometimes with fatal results.[12]

Monochloramine has been shown to be an irritant to eyes and the upper respiratory system and can cause "inflammatory emphysema" in animals.[13] Drinking water containing high levels (ca. 38 ppm) of monochloramine was found to affect macrophage function in rats. The authors noted that this level is about 28 times that expected to occur in treated wastewater and that the compound is "not particularly acutely toxic to the rat immune system at relevant concentrations".[14] Reduced blood cell counts were observed for rats

given water containing monochloramine (1-100 mg/L).[15] This finding was corroborated by another group of researchers who noted that hypochlorous acid and monochloramine are membrane-permeable and highly reactive oxidizing and chlorinating reagents but have little or no mutagenic activity.[10]

A study on the effect of inhalation exposure to $NCl_3$ on rats found a median lethal concentration of 112 ppm (95% C.L., 107-117 ppm).[16] Animals exposed to lower (58 ppm) concentrations survived but showed immediate weight loss and labored breathing. The aerosol had been bubbled through carbon tetrachloride ($CCl_4$) and the UV absorbance measured to arrive at an estimate of exposure (vide infra).

Background

Chloramines are formed when "free chlorine" [chlorine ($Cl_2$), hypochlorous acid (HOCl), or hypochlorite ($OCl^-$)] reacts with available nitrogen compounds, such as ammonia or amines.[17,18] In the chlorination of water, hypochlorous acid is formed:

$$Cl_{2\ (aq)} + H_2O = H^+ + Cl^- + HOCl \quad [K = 4.66 \times 10^{-4}] \qquad (1)$$

(Water saturated with chlorine gives 0.030 moles hypochlorous acid per liter.) A diagram showing the availability of free chlorine is given as Figure 1. At most pH levels of concern in water treatment, only HOCl and $OCl^-$ are found at equilibrium. Both chlorine and hypochlorous acid can react with nitrogen compounds.[6,18] The main pathway for monochloramine formation is:

$$HOCl + NH_3 = H_2O + NH_2Cl \qquad (2)$$

The monochloramine formed can subsequently react, in acidic solution to form trichloramine:[18-21]

$$2NH_2Cl + H^+ = NHCl_2 + NH_4^+ \quad (3)$$

$$3NHCl_2 + H^+ = 2NCl_3 + NH_4^+ \quad (4)$$

and in basic solution to revert to ammonia:

$$3NH_2Cl + 3OH^- = NH_3 + N_2 + 3H_2O + 3Cl^- \quad (5)$$

There are other competing reactions, such as the formation (and subsequent degradation) of hydrazine.[22] Under normal conditions of water treatment, monochloramine ($NH_2Cl$) predominates at pH 8.5 and above, dichloramine ($NHCl_2$) is formed at pH 3 to 5, and trichloramine ($NCl_3$) is formed below pH 3. While mono- and dichloramine are hydrophilic, $NCl_3$ is hydrophobic and is readily evolved from aqueous solution upon aeration.

In water treatment, free chlorine is introduced into the output stream after chlorine demand has been satisfied (see Figure 2). In the introduction of chlorine to ammonia-containing waters, chlorine is first bound to ammonia to form chloramines (area "A"). Additional chlorine then completes the formation of $NCl_3$ and, in a competing reaction, $N_2$, which are evolved from the solution. The completion of these reactions is said to occur at point "B", the "breakpoint". Beyond this point (area "C"), all chlorine that is added yields free chlorine.

There are three principle approaches to treating water: breakpoint chlorination, superchlorination, and chloramination. In breakpoint chlorination, chlorine is first added to reach the breakpoint. An additional amount is then added to yield the desired free chlorine level. This procedure presumes that the water has a constant "chlorine demand" (the amount of chlorine needed to reach breakpoint). Superchlorination is more commonly used because it does not presume a constant chlorine demand. In this procedure, chlorine is added beyond the breakpoint to yield "free chlorine". This

eliminates all nitrogen-containing compounds as $N_2$. Sulfur dioxide ($SO_2$) is then added to destroy the free chlorine, thereafter, chlorine is added to yield the desired free chlorine residual. Chloramination is similar to superchlorination in that chlorine is added to beyond the breakpoint and then reduced with $SO_2$. Then ammonia is added to the water and chlorine is added to yield monochloramine. The monochloramine, although less effective than $Cl_2$ or HOCl for disinfection, is longer lived than either of the other two species in municipal water distribution systems. In addition, the use of chloramination eliminates the formation of halogenated species, such as chloroform in drinking water supplies.

In the past, worker exposures to chloramines have been suspected in poultry processing plants.[3,4] Other potential exposure environments include potato, egg, and hide processing plants. In swimming pool and poultry processing environments, large amounts of organic amines can be present to form monochloramines, which can readily react further to form the di- and trichloramines. The formation of monochloramine is the rate-determining step. Since in many of these environments chlorine demand is not monitored, the irritant $NCl_3$ may be inadvertently produced when chlorine demand changes.

## Analytical Methods

A number of researchers have investigated the analysis of the inorganic chloramines in water, including the American Water Works Association (AWWA).[23] There are five wet chemistry methods for "free chlorine": ortho-toluidine (OT), methyl orange, leuco crystal violet (LCV), syringaldazine (FACTS), and N,N-diethyl-p-phenylenediamine ferrous ammonium sulfate titrimetric (DPD) methods.[18,23] The OT and DPD methods are able to classify

the chlorine present as either chloramine or "free chlorine". The other methods rely on the nonselective oxidation of the indicator and thus are not useful in the determination of the inorganic chloramines in the presence of hypochlorous acid or molecular chlorine. The DPD method is preferred to differentiate the inorganic chloramines from "free chlorine".[24,25]

Some investigators have noted problems with the DPD method when applied to systems like swimming pools.[26-28] Chlorinated creatinine, a constituent of urine, is reported to appear in the DPD method as $NCl_3$.[26] This was confirmed by other researchers who noted that organic chloramines also interfere.[27,28] This implies that even the results of the DPD measurement of the parent water may be biased in the presence of compounds, such as chlorinated creatinine, likely to be present in the water of a municipal swimming pool or poultry processing plant.

Ultraviolet (UV) absorbance has been used to determine the content of the inorganic chloramines in water.[29-32] Monochloramine solutions were found to absorb at 243 nm and obey Beer-Lambert Law over the range $5 \times 10^{-4}$ to $3 \times 10^{-3}$ M.[29] Mono-, di, and trichloramine in carbon tetrachloride could be determined by measurement of the solution's absorbance at 265 nm, 300 nm, 335 nm, and 345 nm (Figure 3).[30] This procedure was patented for determination of $NCl_3$ in an isocyanurate process stream, which compared the absorbance at 218 nm with that at 260 nm.[31] Another researcher expanded the use of UV absorbance for the continuous-flow simultaneous determination of the inorganic chloramines in water.[32]

Organic and inorganic chloramines have been determined electrochemically as well.[33-35] Monochloramine and chlorine could be determined by measuring the current at +0.20 V vs Ag/AgCl in a flow-injection system.[33] This was

extended to include the analysis of mono- and dichloramine in water by amperometric determination at -0.11 and -0.34 V vs Ag/AgCl.[34] A potentiometric stripping analysis on a copper substrate for the determination of parts per billion (ppb) of monochloramine or hypochlorous acid in aqueous solutions was proposed by another researcher.[35] Selectivity was obtained by comparing the results of determinations made at pH 2.5 with those made at pH 6.

Organic chloramines have been analyzed by liquid chromatography after derivitization.[36-38] Chloramines could be converted into highly fluorescent dansyl derivatives by their reaction with 5-(dimethylamino)naphthalene-1-sulfinic acid.[36] Chloramines at concentrations of $10^{-4}$ M and above could be analyzed directly; lower concentrations needed to be preconcentrated. Comparable results were found using the reagent dansylsulfinic acid.[37] The derivative 2-mercaptobenzothiazole was found to yield sulfenamides when reacting with chloramines.[38] These could be analyzed by UV or electrochemical detection.

Mass spectrometry has been applied for the determination of the inorganic chloramines in water.[39-42] Early work showed that the $NCl_3$ was stable enough to be introduced into a mass spectrometer after aging the system.[39] Ions were observed at m/z 35 ($Cl^+$), 49 and 51 ($NCl^+$), 84, 86, and 88 ($NCl_2^+$), and a small peak at 119 ($NCl_3^+$) at 77 eV. Nitrogen trichloride was found to pass through a cross-linked silicone hollow fiber membrane into the source of a mass spectrometer, where it could be analyzed in real-time.[40] The increase of intensity at m/z 84 ($NCl_2^+$) with an increase in intensity of the ions at m/z 119 and 121 without an increase in intensity at m/z 117 (due to chlorinated hydrocarbons, $CCl_3^+$) was used to determine the formation of $NCl_3$. This procedure was then applied to the analysis of organic and

inorganic chloramines in water with the use of a dimethylvinyl silicone membrane.[41,42]

The infrared spectra of the inorganic chloramines have been obtained by dispersive instruments.[43] The absorbance bands for these compounds are given in Table I. Ammonia bands were reported to overlap those of monochloramine and dichloramine was not able to be detected without the presence of monochloramine. Sample stability of the inorganic chloramines was reported to be a problem; no sample remained for longer than 20 minutes. Another group of researchers observed a band for $NCl_3$ at about 650 $cm^{-1}$, but not those at 1021 and 1273 $cm^{-1}$, and ascribed these latter bands to impurities present in the original work.[39] Nitrogen trichloride in $CCl_4$ and in hexane was found to have bands somewhat shifted (Table II).[44-46]

At present there is no sampling and analytical method for the determination of the inorganic chloramines in air. However, a few researchers have proposed approaches to the problem. One researcher has collected air samples into a cold trap containing $CCl_4$ kept at -10 °C to 0 °C.[30] The sample was warmed to ambient temperature, diluted to volume, and analyzed by UV spectroscopy. Recently, a NIOSH researcher investigated the potential for a sampling and analytical method.[47] This was prompted by a health hazard evaluation (HHE) request at a poultry processing plant where workers were complaining of acute irritation, presumably due to $NCl_3$.[5] It was noted that $NCl_3$ might be analyzed by one of four procedures:

1. Collect an air sample at -10 °C to 0 °C in $CCl_4$ and measure UV absorbance of the solution at 265 nm. The detection limit was estimated at 2 ppm for a 60 L sample.

2. Collect an air sample in an impinger containing a methyl orange

solution at pH 3 and measure UV absorbance of the solution at 510 nm.

3. Collect an air sample in a gas cell and measure the UV absorbance of the vapor.

4. Collect an air sample in a gas cell and measure the IR absorbance of the vapor.

The first three procedures are not satisfactory. The first procedure requires sampling using a medium that is more hazardous than the analyte (as $CCl_4$ is a carcinogen). The collection efficiency and stability of $NCl_3$ have not been demonstrated. Further, there is concern that ice may form in the impinger upon sampling in the humid environments. The second procedure, which relies on bleaching of the indicator, is not specific for chloramines. The unavailability of a gas cell for UV analysis of chloramine aerosol nullified the third approach. Regarding UV analysis, in addition to the points mentioned, the technique is unlikely to yield a low enough detection limit to observe ambient levels (about 4 ppm, where eye irritation is reported to be observed[5]) of chloramines. With the advent of portable Fourier transform infrared spectrophotometer (FT-IR) instruments, infrared analysis may be a feasible approach.

Because of the transient nature of the compounds and the rapid equilibrium established between the species dependent on the pH of the solution, only a direct analysis technique (as opposed to a laboratory-based procedure) would give information on the relative species present in the environmental aerosol. The DPD method addressed earlier is still the best method available for the determination of the relative inorganic chloramines in water, despite its limitations. It could be used to get information on the species present in the pool water, but would have to be performed on-site

because of the instability of the compounds in question.

Some direct reading instruments were readily excluded from consideration. Discussions with a researcher familiar with ion mobility spectrometry[48] noted that the inorganic chloramines would likely only give a chloride ion, as do the majority of chlorinated organics, and thus not prove useful for their determination. In addition, all gas chromatographic techniques were excluded because of the thermal instability of the compounds.

Of the remaining techniques capable of yielding direct analysis (UV, FT-IR, and mass spectrometry), FT-IR was believed to offer the best potential for success given the types of environments that are of interest. FT-IR is capable of speciating the inorganic chloramines, based on the work noted above. Unlike UV instruments, sufficient resolution is available with most FT-IR instruments so that closely spaced bands have the potential for being resolved. Mass spectrometers usually cannot tolerate the levels of water present (high humidity) in these environments, owing to limitations such as pump capacity and pressure broadening of the ions (which reduces resolution). However, a researcher at Oak Ridge National Labs (ORNL) has been investigating sample inlets for mass spectrometers that would be amenable for direct atmospheric sampling, even in high humidity environments.[49,50] If the ORNL research is successful, a mass spectrometric procedure for chloramines may become viable.

## Experimental

Infrared scans were taken on a Nicolet 60SX Fourier transform infrared spectrophotometer (Nicolet Analytical Instruments, Madison, WI) with a deuterated triglycine sulfate (DTGS) detector and KBr beamsplitter. Gas

samples were examined using a 10-PA (Infrared Analysis Inc., Anaheim, CA) ten meter fixed path gas cell. The internal metal transfer line was replaced with a polytetrafluoroethylene (PTFE) tube and the mirrors of the cell were coated with gold to prevent reaction with any nitrogen trichloride produced. Attenuated total reflectance (ATR) measurements employed a CIRCLE (Spectra-Tech Inc., Stamford, CT) cylindrical internal reflectance cell. A Hewlett-Packard Model 8542A Diode Array Spectrophotometer (Hewlett-Packard, Palo Alto, CA) was used to collect all UV-visible spectra. The instrument collected spectra from 190 to 800 nm over a 10 second collection time.

Mass spectrometry was performed on a VG Model 7070HS mass spectrometer (VG Analytical, Manchester, England) with a VG Model 2250 data system. Electron impact measurements were made at 70 eV with the emission current maintained at 500 $\mu$A. The inlet and source temperatures were maintained at 80 °C. For full scan mass spectra, the mass spectrometer was scanned from 340 amu to 25 amu every 2 seconds with resolution adjusted to 2000. The selected ion monitoring (SIM) analysis mode using voltage switching was employed for multiple-ion detection at a resolution of 3000. The mass spectrometer accelerating voltage was calibrated over the mass range 130 to 80 with perfluorokerosene ions at m/e 130.990 and 92.995 used for system background references. The parent ion, $NCl_3$+ (m/e 118.900 and 120.900) and primary ion, $NCl_2$+ (m/e 83.940 and 85.930) of $NCl_3$ were used for all observations. Chlorine was indicated by the presence of its molecular ion at 71.937.

Ion chromatographic analysis was performed on a Dionex Model 4000i instrument (Dionex Instruments, Sunnyvale, CA) equipped with an AG4A precolumn, ASA4 analytical column, and anion micromembrane suppressor. A

40 mM sodium hydroxide eluant was pumped at 1.5 mL/min yielding a retention time for chloride ions of 1.57 to 1.63 minutes. Samples were compared to standards prepared from high purity potassium chloride with concentrations from 0.05 to 10 $\mu g$ $Cl^-$/mL.

Initial infrared spectrophotometric experiments involved generation of a chloramine aerosol and its observation in a gas cell. The system was set up in a closed loop to facilitate the generation of a steady-state concentration in the gas cell. This generator was first evaluated with various concentrations of sulfur hexafluoride ($SF_6$) in nitrogen. The $SF_6$ was found to give linear absorbance in the gas cell over the concentration range 3.6 to 36 $mg/m^3$. A concentration of 8.4 $mg/m^3$ $SF_6$ was shown to be an acceptable internal standard with no absorbances which would interfere with the determination of any of the inorganic chloramines. After purging the system with nitrogen, a small amount (0.74 gm) of trichloroisocyanuric acid, which releases $NCl_3$ when hydrolyzed, was placed into the generation flask along with 200 mL of chlorine demand-free water. The mixture was then stirred to release any $NCl_3$ from the solution. A pump moved the vapor into the gas cell for spectroscopic examination for traces of $NCl_3$ or other chloramines.

Next, a monochloramine solution was placed into the generation system, which had been purged with nitrogen, and the solution stirred to evolve chloramines from solution. Sulfur hexafluoride was added as a tracer gas to allow independent scans to be compared. The FT-IR spectrum of the vapor was taken. Samples of the vapor were also taken with a gas-tight syringe and examined by mass spectrometry. Hydrochloric acid (6N) was then added into the monochloramine solution to drive the equilibrium toward the formation of $NCl_3$. After allowing a short (3 minute) equilibration period, the FT-IR spectrum of

the vapor was taken and compared to the background (initial scan). As before, samples of the vapor were taken and examined by mass spectrometry. Ammonia and chlorine vapor were examined as potential interferences.

Chloramines in water were examined by FT-IR using a CIRCLE internal reflectance cell. This approach employed attenuated total reflectance of an IR beam through a crystal in direct contact with the solution of interest to obtain the IR spectrum. Instead of a circulating vapor, an aliquot of the monochloramine solution was placed into the CIRCLE cell and scanned. As in the above experiment, 6N hydrochloric acid (HCl) was added to the monchloramine solution to drive the monochloramine to $NCl_3$. After addition, an aliquot was taken and scanned in the cell.

These experiments were then replicated with hexane extracts of the aqueous solutions. A monochloramine solution was prepared as before and divided into two 100-mL aliquots. One hundred milliliters of the solution were then placed into a separatory funnel, 5 mL of hexane added, and the mixture shaken. After the aqueous portion was removed, the hexane extract was poured off, placed in a glass vial, and capped. Ten milliliters of 6N hydrochloric acid were added to 100 mL of the remaining monochloramine solution to drive the monochloramine to $NCl_3$. This solution was extracted with 5 mL of hexane. Both extracts were then examined by FT-IR in the CIRCLE cell.

A monochloramine solution was prepared, and 50 mL aliquots placed into separate flasks to which was added either 10 mL of chlorine solution (1:10 dilution of saturated chlorine water), 25 mL chlorine solution, 5 mL of 6N HCl, or 10 mL of 6N HCl. Each of these solutions, in addition to an aliquot of the unfortified monochloramine solution, was then extracted with 5 mL of

hexane and examined by UV-visible spectrometry. This examination of hexane extracts of the monochloramine was performed to determine the conditions needed for complete conversion to $NCl_3$.

The stability of $NCl_3$ in hexane was also examined. Nitrogen trichloride solutions were prepared by addition of 40 mL of 6N HCl to 200 mL of monochloramine solution. This solution was then extracted with 10 mL of hexane. A 1-mL aliquot of this extract was taken and placed in a 10 mL volumetric flask and brought to volume with hexane. This was repeated to yield a 1:100 dilution. These extracts (parent, 1:10, and 1:100 dilutions) were then examined by UV spectrometry over a 7 day period.

Solid sorbents were examined in combination with FT-IR and mass spectrometry. Silica gel tubes (ORBO-53, Supelco, Bellefonte, PA, part number 2-0265), which do not collect chlorine, were examined for collection of $NCl_3$, as were silver membrane filters (0.45 μm pore size, Poretics Corp., Livermore, CA, part number 51033), which are used in Method 6011 for halogen gases.[51] A silver membrane filter was investigated as a possible prefilter, which would remove $Cl_2$ and not $NCl_3$, with a detector tube (Chlorine 0.2/a, Draeger, Lubeck, Germany, part number CH 24301) behind the filter to react with any $NCl_3$ present in the environment. Nitrogen trichloride prepared for the above FT-IR vapor studies were sampled with both silica gel and silver filter samplers (two samples were taken for both the parent and diluted [1:200] aerosol) through the use of personal sampling pumps. The samples were desorbed (silica gel with 10 mL of deionized water; silver filter with 3 mL of 6 mM sodium thiosulfate) and analyzed for chloride by ion chromatography. The reactivity of detector tubes to $NCl_3$ was also examined. Potential breakthrough of $NCl_3$ and chlorine through silver membrane filters was examined

by mass spectrometry. Nitrogen trichloride vapor (with an $SF_6$ internal standard) in a glass/PTFE sample bulb, which was sheathed in aluminum foil to protect the contents from light, was drawn through silver membrane filters and vapor samples were taken before and after the media. Similarly, chlorine breakthrough was examined with a bubbler of saturated chlorine water as the $Cl_2$ source.

The final experiments examined the stability of $NCl_3$ aerosol in a glass/PTFE sample bulb with mass spectrometric analysis. Nitrogen trichloride aerosol was prepared as before and a gas tight syringe was used to transfer about 20 mL of the $NCl_3$ vapor into a 250 mL glass/PTFE sample bulb containing approximately 7.7 $mg/m^3$ $SF_6$ tracer gas. The bulb was sheathed in aluminum foil to protect the contents from light. Samples of the resulting mixture were taken with a gas-tight syringe over a 48 hour period and injected through an injection port placed directly before the source in the mass spectrometer. The parent ion ($NCl_3^+$) or primary ion ($NCl_2^+$) of $NCl_3$ was then monitored in addition to the primary ion of the sulfur hexafluoride internal standard. The experiment was then replicated but with the addition of primary amines (1 $\mu$L of 1,2-dimethylpropylamine and 3 $\mu$L of n-butylamine) after 28 and 44 hours, respectively. The bulb was monitored by means of mass spectrometry for over 24 hours to check on initial stability, and then the vapor and liquid amine injections were made to determine the effect of amine interferences on $NCl_3$ stability.

## Results and Discussion

The investigation helped to clarify the proposals for analytical methods offered previously and eliminate non-viable approaches for the determination

of chloramine aerosols. The experiments confirmed the need for a direct reading instrumental approach for analysis.

Initial work with infrared spectrometry indicated that $NCl_3$, evolved from hydrolysis of trichloroisocyanuric acid, could be detected in the gas phase (Figure 4). When a monochloramine solution was introduced and then acidified to produce $NCl_3$, the only band observable in the IR spectrum was at 650 $cm^{-1}$ (from $NCl_3$). This band, which is very broad (ca. 30 $cm^{-1}$ wide), can be seen in atmospheres low in carbon dioxide (Figure 5). When high concentrations of $NCl_3$ were generated, however, the optics of the FT-IR gas cell were readily coated with a white powder film. This indicates that the use of FT-IR at these concentrations is a "one-shot" approach, and would thus not be useful in the field. At the lower concentrations expected to represent typical exposures, the sidebands of carbon dioxide around its absorbance band at 666 $cm^{-1}$ completely obscure the 650 $cm^{-1}$ band of $NCl_3$ (Figure 6). Thus, FT-IR (either laboratory-based or portable) cannot be used for analysis of ambient $NCl_3$.

Aqueous solutions of monochloramine (ca. 500 $\mu g/mL$) did not yield any observable absorbance bands when examined by attenuated total reflectance using the CIRCLE cell in the FT-IR. Examination of the same solution when acidified to yield $NCl_3$ also failed to provide any observable absorbance bands. This also proved to be the case when the experiments were replicated with hexane extracts of the solutions.

The UV absorbance spectra of the hexane extracts of monochloramine and $NCl_3$ (Figure 7,8) were comparable to those reported in the literature.[30] Addition of 6N HCl in a 1:10 ratio to monochloramine (ca. 500 $\mu g/mL$) was found to yield complete conversion to $NCl_3$. Addition of chlorine solution, even at

a ratio of 1:2, was not as efficient in effecting complete conversion.

$NCl_3$ could still be observed in the parent and 1:10 diluted hexane extracts 4 days after generation, however both were found to degrade over a one week period (Figure 9,10). No differences in response of the 1:100 dilution were observed over the same four days at the analytical wavelength, 344 nm (Figure 11). This indicates that there may be an interaction between the variables of concentration and storage time. A plot of absorbance at 344 nm versus time for both parent and 1:10 diluted concentrations shows a comparable decline, indicative of first-order decay (Figure 12). This indicates that any quantitative determination would require information on the elapsed time between sampling and analysis.

Solid sorbents were not effective for the collection of $NCl_3$. $NCl_3$ was found to break through silica gel tubes below 24 $\mu g$ $Cl^-$ and any hydrochloric acid formed by the hydrolysis of $NCl_3$ would interfere. Mass spectrometric analysis indicated that silver filters reacted to some degree with $NCl_3$ but did not remove all the $NCl_3$. However, the sensitivity was too poor to allow estimates of the percentage that might have reacted. When $NCl_3$ vapor was placed into a glass/PTFE sample bulb and sampled with a detector tube behind a silver filter, the detector tube turned color almost immediately. (It should be noted, however, that $NCl_3$ cannot be formed without some molecular chlorine being present.) This indicated that either the silver filter did not collect all the chlorine and that this residual chlorine passed through the silver filter and reacted with the detector tube, or that the silver filter had no capacity for $NCl_3$ (but did for chlorine gas) and that this $NCl_3$ passed through the silver filter and reacted with the detector tube. Mass spectra of samples downstream of the detector tube showed significant amounts of $SF_6$ tracer with

no detectable amount of $NCl_3$, indicating that $NCl_3$ was reacting with the o-tolidine in the detector tube. Examination of the generated $NCl_3$ by mass spectrometry showed the presence of chlorine gas.

When chlorine vapor from a bubbler filled with saturated chlorine water was passed through a sample train of a silver membrane filter followed by a detector tube, breakthrough of chlorine occurred in under 350-390 $\mu$g Cl. This estimate of breakthrough was determined from analysis of chlorine on the silver filters at the first appearance of color change (reaction) on the detector tube. Complicating any estimate of breakthrough was the problem of chloride being found in the blank desorbed silver filter samples. It was found that the sodium thiosulfate solution used to desorb the filters contains chloride as an impurity. Discussion with representatives from a number of vendors that supply the chemical indicate that this impurity is not monitored in their commercial products. To arrive at an estimate for chlorine which reacted with the silver filter, an estimate of chloride from the blanks had to be subtracted. These blanks averaged 1.8 $\mu$g but were quite variable (77% RSD).

Mass spectrometry did provide a possible approach for analysis of air samples for $NCl_3$. While Tedlar bags were not found to be effective storage containers for "grab" samples, sample bulbs constructed of glass and PTFE were useful. The use of commercially available SUMMA canisters, which are made from passivated stainless steel, had not been evaluated. (It remains to be seen, however, whether $NCl_3$ would react with the passivated metal surface.) Gaseous $NCl_3$ was found to be stable in a glass/PTFE sample bulb for over 48 hours (Figure 13,14). The parent ion of $NCl_3$ could be seen in both the concentrated vapor and in dilutions of up to 1:1000 using high resolution mass

spectrometry with injection of the vapor into an inlet at the GC transfer line to the instrument. Ion intensities were found to be variable, in part owing to problems with gas-tight syringes, but even after ratioing the ion intensity of $NCl_3$ to that of $SF_6$ to account for the actual volume introduced, the relative standard deviation was high (up to 44%). This indicates that sample introduction into the mass spectrometer is a problem that would need to be resolved before any quantitative work could be performed.

Nitrogen trichloride vapor was found to be stable in the presence of amines. When samples of the primary amines 1,2-dimethylpropylamine and n-butylamine were introduced (as liquids), the $NCl_3$ parent ion could be observed in their presence (Figure 15,16). In fact, the ion intensity of the $NCl_3$ did not appreciably change from that found prior to their introduction (Figure 17). As before, significant scatter in the intensities precluded unambiguous interpretation, but in all cases the parent ion of $NCl_3$ could be easily observed.

Recent work by researchers at the Oak Ridge National Laboratory (ORNL) in "Direct Sampling Ion Trap Mass Spectrometry" found that a number of organic compounds could be monitored in real-time in environmental matrices.[52-55] Their work, which employed a Finnigan MAT Model ITS-40 mass spectrometer for field applications, was able to determine organics such as benzene and trichloroethylene at parts per billion levels. The system was able to scan the mass range 15-650 amu and generate a mass spectrum every 100 milliseconds. A combination molecular drag pump and diaphragm pump replaced the rotary vacuum pump normally used and lowered the power requirements of the system to 550 watts. They designed a custom fixed-ratio open split capillary restrictor interface for atmospheric sampling. This interface passes only a small (1%)

portion of the sample through to the mass analyzer. Their system does suffer from isobaric (same mass) interferences as their system is not high resolution. Incorporation of their interface to portable instruments having higher resolution may provide for a direct analysis procedure for the determination of nitrogen trichloride.

## Conclusions

A direct sampling and analysis approach for the determination of inorganic chloramines is the only viable strategy, based on the limited stability of these compounds. Attempts to employ solid sorbent samplers for the inorganic chloramines were not successful. The materials either were not specific for chloramines or had a very limited capacity. In all cases, the analysis required chloride to arise solely from the chloramines and not from other sources. An approach involving FT-IR determination failed because the presence of atmospheric levels of $CO_2$ caused almost total absorbance over the only useable analytical bandwidth of $NCl_3$.

The collection of a "grab" sample with subsequent laboratory determination by mass spectrometry, within 48 hours, was shown to be feasible, at least qualitatively. The presence of amines in the grab sample was found not to change the amount of $NCl_3$ vapor present over the time scale examined. However, $NCl_3$ was found to decay over time, even without the presence of reactive chemicals. This underscores the need for an on-site (direct) analysis procedure.

It is recommended that any further work on mass spectrometric analysis of $NCl_3$ in workplace environments be investigated as part of the ongoing research on field portable instrumentation. This research would need to

address the losses of $NCl_3$ during sampling and the consequent variability of ion intensities presently found. The use of the fixed-ratio split inlet investigated by researchers at ORNL may provide a mechanism for the introduction of the $NCl_3$ aerosol into the mass spectrometer. A successful procedure for the determination of $NCl_3$ by portable mass spectrometry would provide a mechanism for real-time monitoring of this potential workplace hazard.

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TABLE I
INFRARED ABSORBANCES OF THE INORGANIC CHLORAMINES[a]

| Compound | Absorption Band, $cm^{-1}$ | (Relative Strength)[b] |
|---|---|---|
| $NH_2Cl$ | 6522.9 | M |
| | 4893.8 | M |
| | 3380.0 | S |
| | 2020 | W |
| | 1553 | S |
| | 1032 | VW |
| | 686 | VW |
| $NHCl_2$ | 6393.9 | M |
| | 3279.0 | VS |
| | 2584 | W |
| | 1960 | W |
| | 1295 | M |
| | 1002 | VS |
| | 687 | S |
| | 666 | S |
| $NCl_3$ | 1273 | W |
| | 1021 | W |
| | 652 | S |
| | (390) | ? |

[a] From J. Amer. Chem. Soc. 74 6076 (1952).
[b](VS, very strong; S, strong; M, medium; W, weak; VW, very weak)

TABLE II

INFRARED ABSORBANCES OF NITROGEN TRICHLORIDE IN CARBON TETRACHLORIDE[a]

| Absorption Band, $cm^{-1}$ | (Relative Strength)[b] |
|---|---|
| 1282 | W |
| 1179 | W |
| 1074 | W |
| 642 | VS |
| 608 | S |
| 538 | W |
| 518 | W |
| 383 | M |
| 350 | W |
| 257 | M |

[a] From J. Chem. Phys. 49 3751 (1968).

[b](VS, very strong; S, strong; M, medium; W, weak; VW, very weak)

FIGURE CAPTIONS:

Figure 1. Form of available chlorine as a function of pH (From "Water Disinfection - Chemical Aspects and Analytical Control"[18])

Figure 2. Residual chlorine form as a function of applied chlorine dose (From "Water Disinfection - Chemical Aspects and Analytical Control"[18])

Figure 3. Ultraviolet absorption of chloramines (From "Determination of Mono-, Di-, and Trichloramine by Ultraviolet Spectrophotometry"[30])

Figure 4. IR vapor phase spectra of $NCl_3$ evolved from trichloroisocyanuric degradation over time (9-42 minutes)

Figure 5. IR vapor phase spectra of $NCl_3$, showing peak at 650 $cm^{-1}$

Figure 6. The same IR spectra of $NCl_3$ as Figure 5, but with the addition of atmospheric levels of $CO_2$

Figure 7. UV spectra of monochloramine in hexane

Figure 8. UV spectra of nitrogen trichloride in hexane

Figure 9. UV spectra of parent solution of $NCl_3$ in hexane, Day 1-7

Figure 10. UV spectra of 1:10 diluted solution of $NCl_3$ in hexane, Day 1-7

Figure 11. UV spectra of 1:100 diluted solution of $NCl_3$ in hexane, Day 1-7

Figure 12. Plot of UV absorbance at 344 nm versus time for parent and 1:10 diluted solutions of $NCl_3$ in hexane

Figure 13. Mass spectra of $NCl_3$ (with $SF_6$ internal standard) after 24 hours [Upper trace: $NCl_3$; Lower trace: $SF_6$]

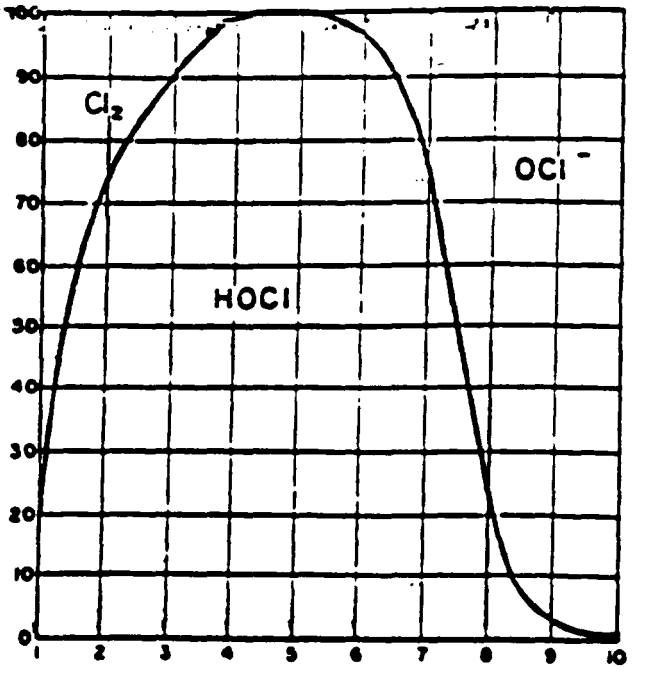
Figure 14. Plot of corrected $NCl_3$ mass spectral intensity versus time

Figure 15. Mass spectra of $NCl_3$ after addition of 1 $\mu$L of 1,2-Dimethyl-propylamine [Upper trace: $NCl_3$; Lower trace: $SF_6$]

Figure 16. Mass spectra of $NCl_3$ after addition of 3 $\mu$L of n-Butylamine [Upper trace: $NCl_3$; Lower trace: $SF_6$]

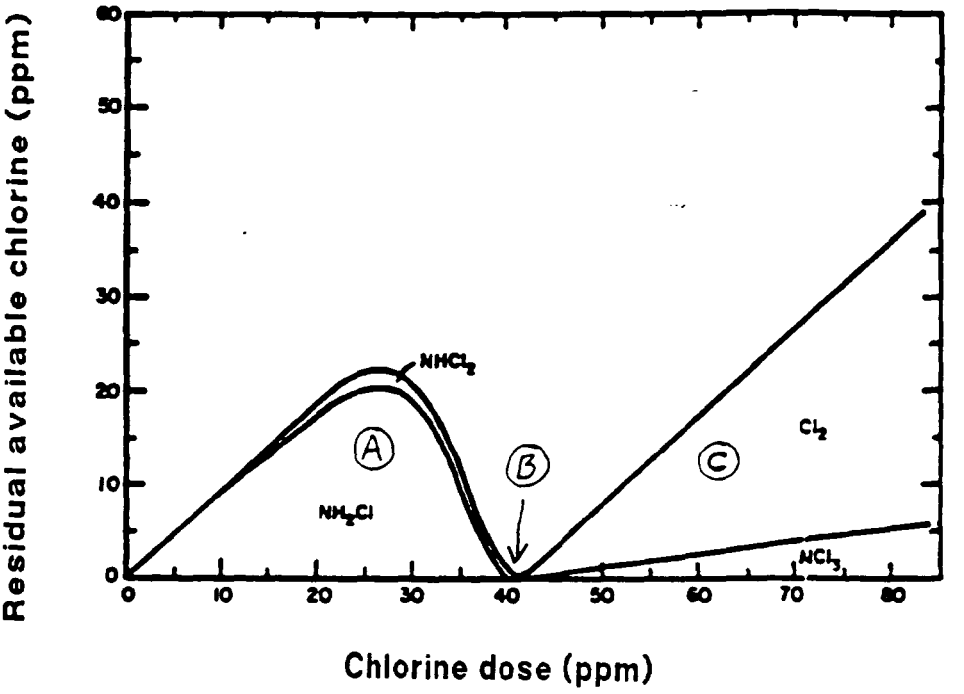
Figure 17. Plot of corrected $NCl_3$ mass spectral intensity versus time, with amine additions [DMPA: 1,2-dimethylpropylamine]

Fig. 1



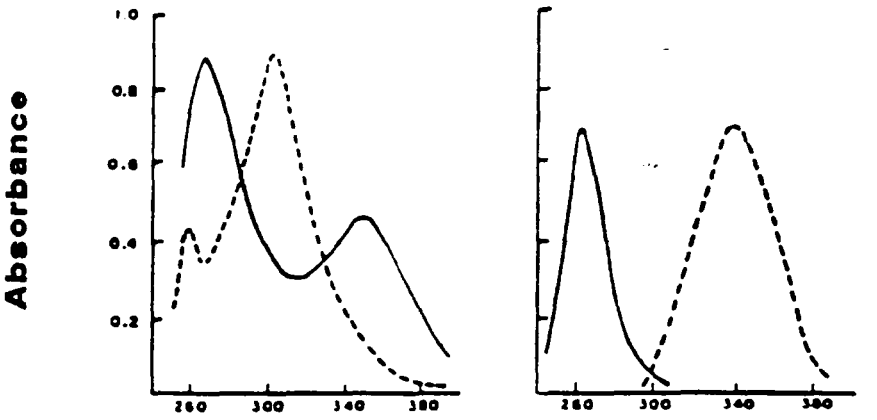

**Effect of pH value on form of free available chlorine in water at 20 °C and less than 100 mg/l dissolved solids**

Fig. 2




Chlorine dose-residual curve at pH 7.0 after 1 day
(Initial ammonia 0.5 ppm)

Fig. 3




**Wavelength (nm)**

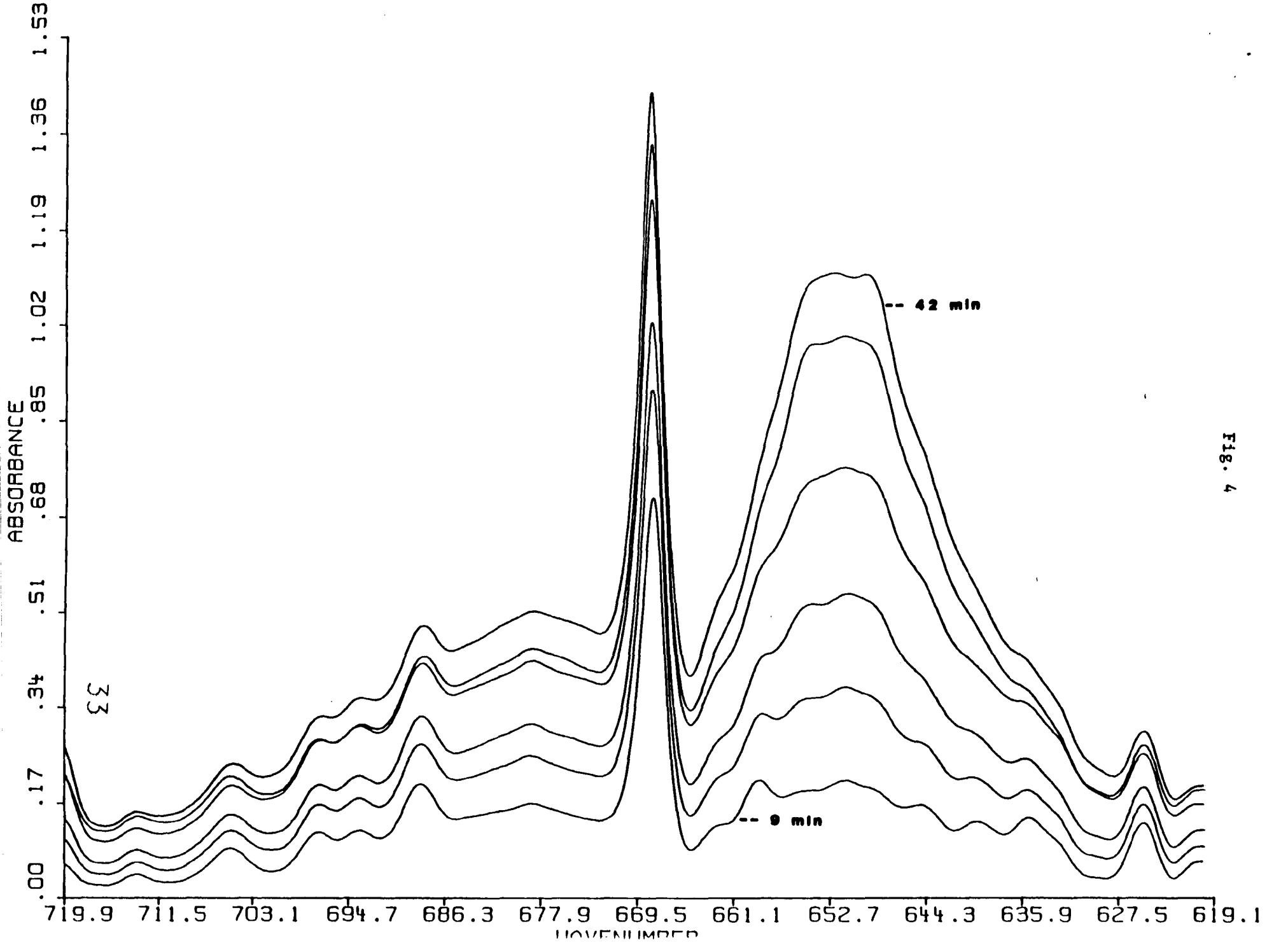
**Ultraviolet absorption of the chloramines and chlorine in $CCl_4$**

Left ---------- Dichloramine

———— Trichloramine

Right ---------- Chlorine

———— Monochloramine


ABSORBANCE
.00
.17
.34
.51
.68
.85
1.02
1.19
1.36
1.53
719.9
711.5
703.1
694.7
686.3
677.9
669.5
661.1
652.7
644.3
635.9
627.5
619.1
-- 42 min
-- 9 min

33

Fig. 4

Fig. 5

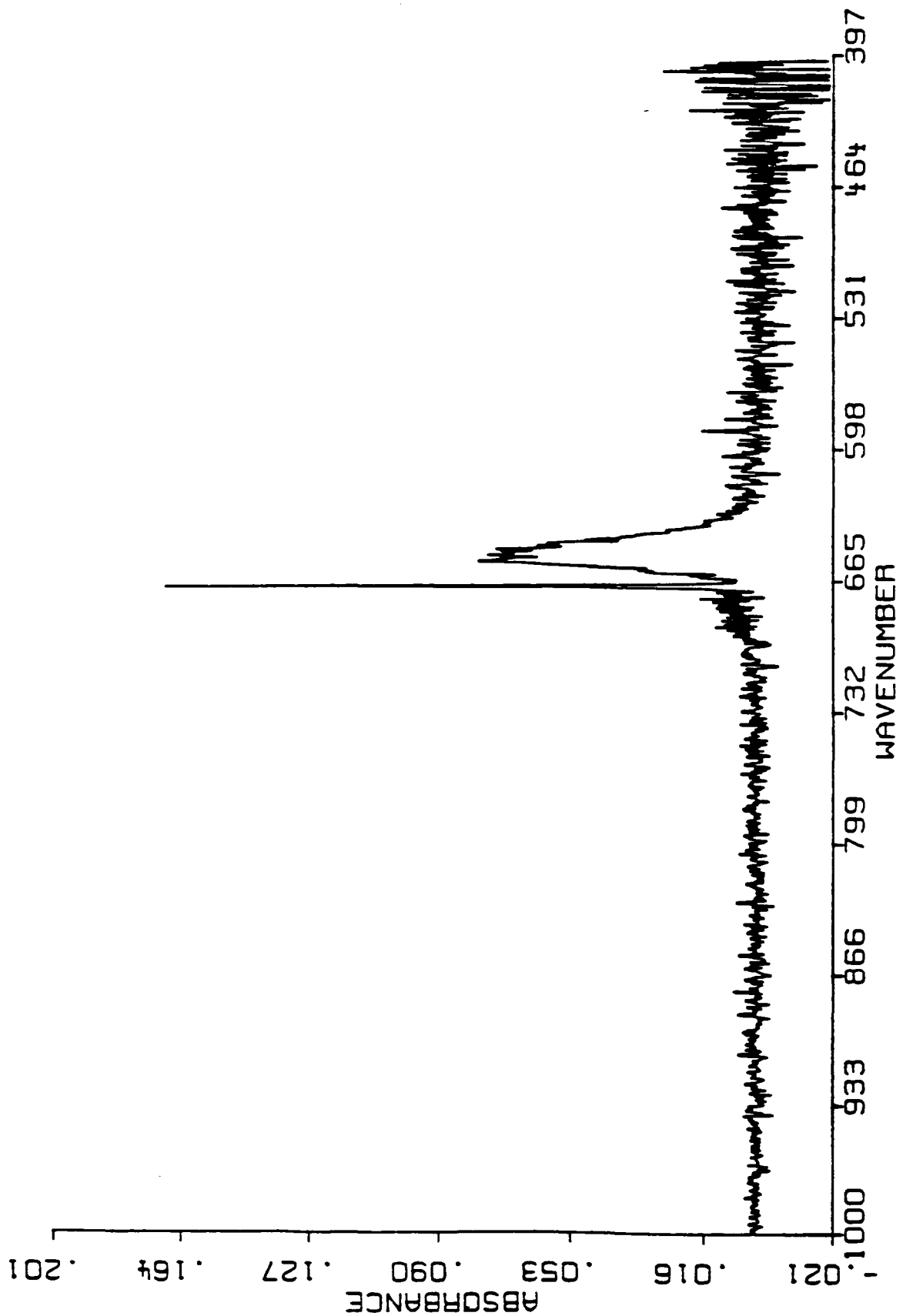
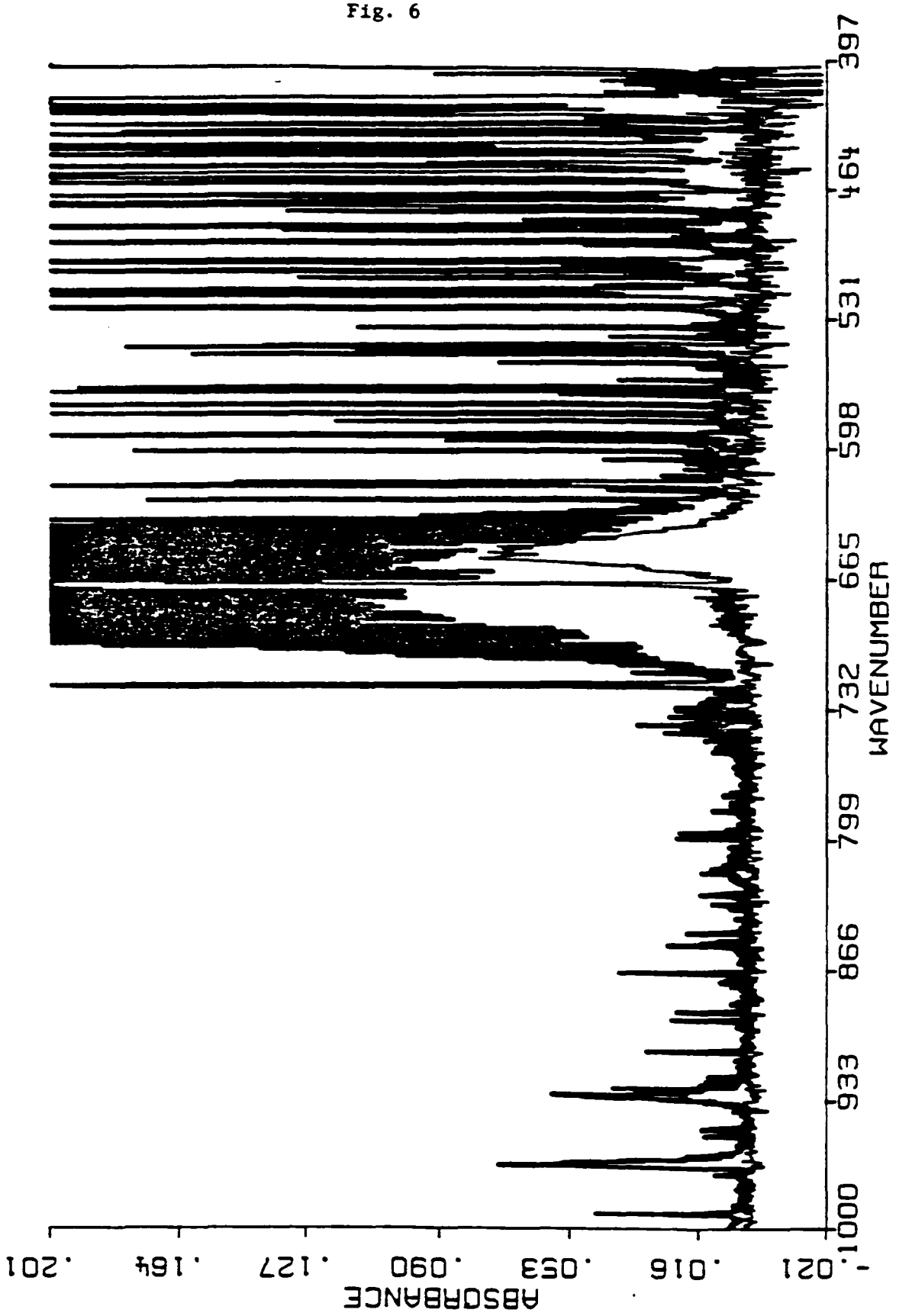

ABSORBANCE
-.021
.016
.053
.090
.127
.164
.201
1000
933
866
799
732
665
598
531
464
397
WAVENUMBER

Fig. 6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.201
.164
.127
.090
.053
.016
-.021
WAVENUMBER
1000
933
866
799
732
665
598
531
464
397

Fig. 7

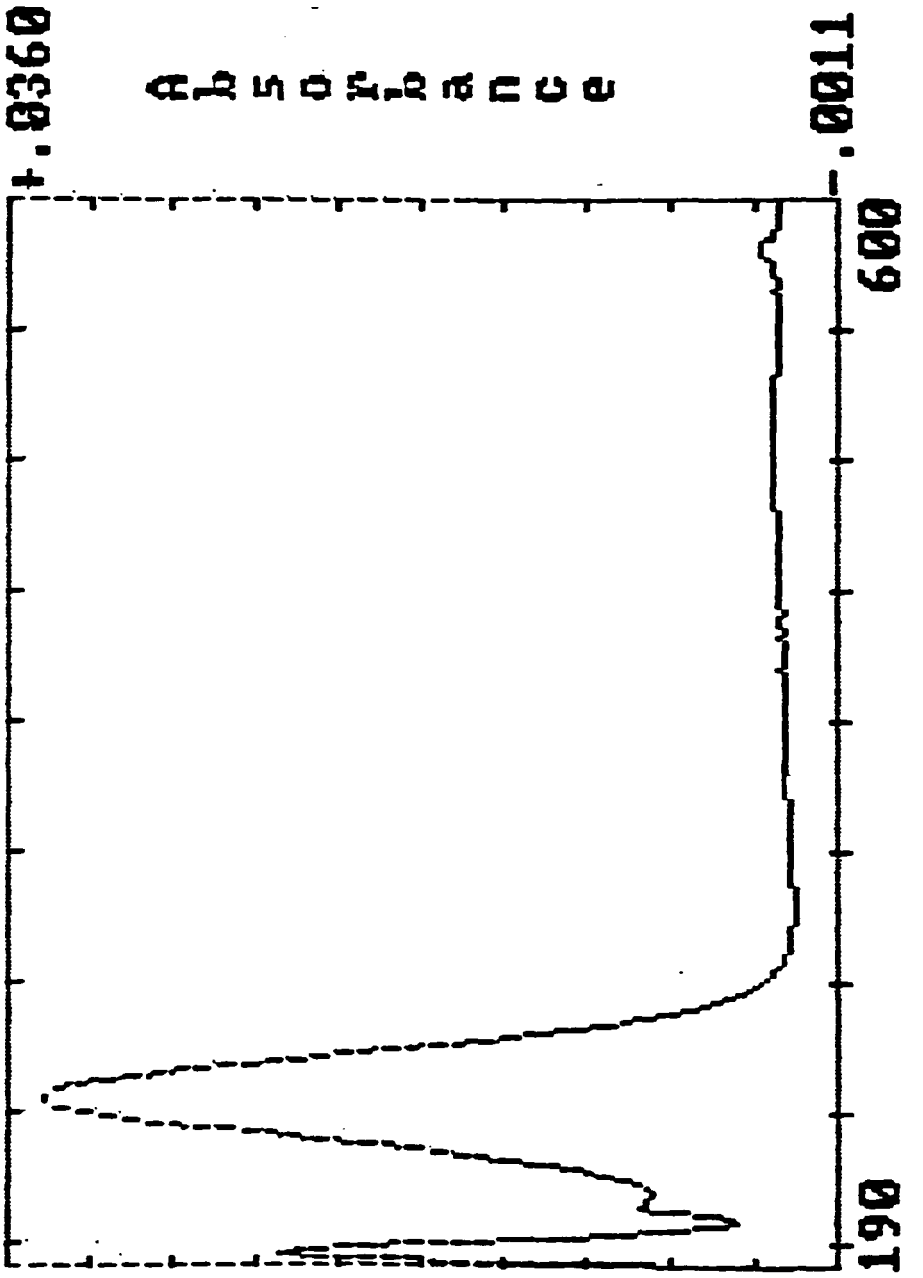


Fig. 8

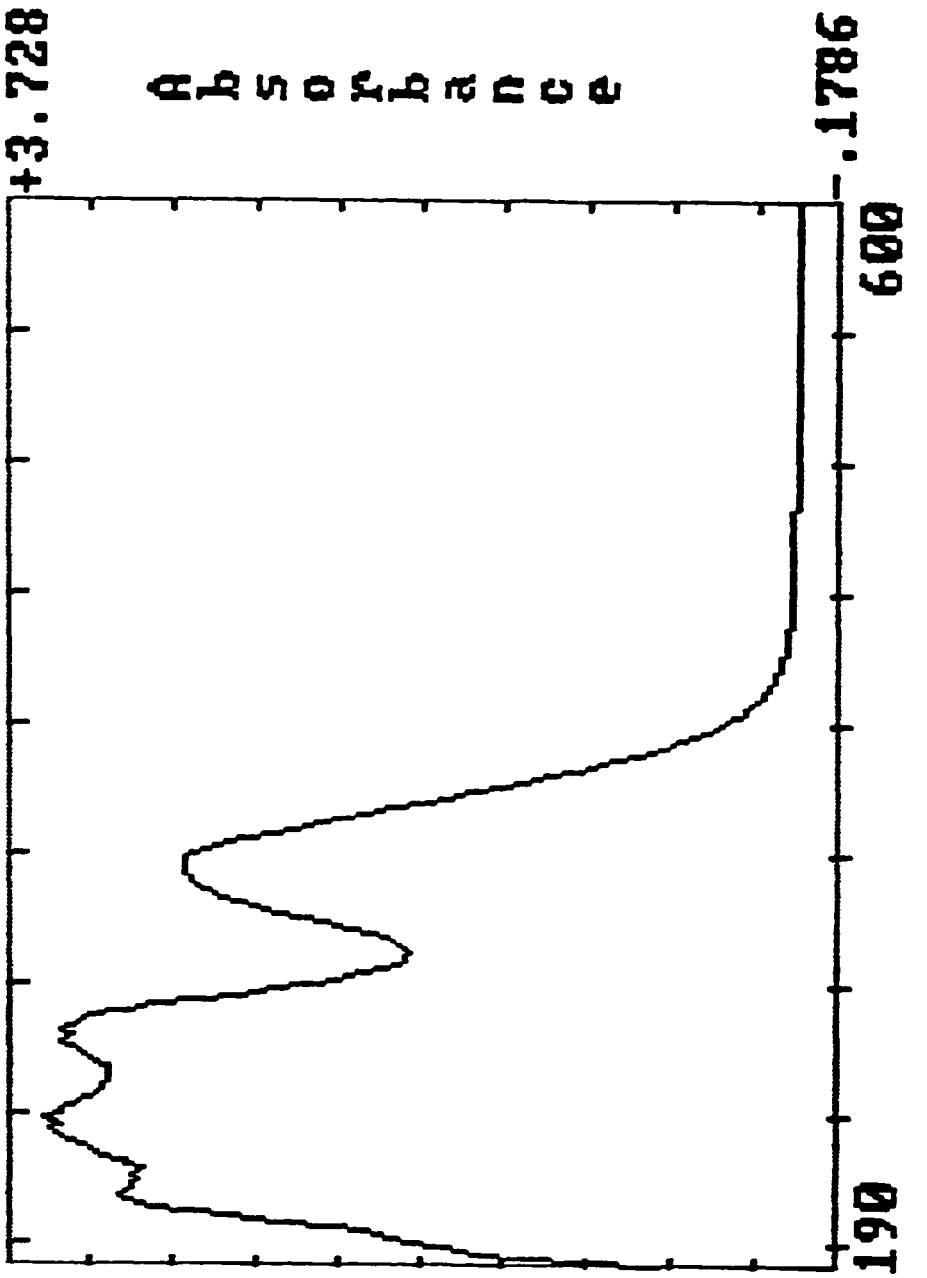


Fig. 9

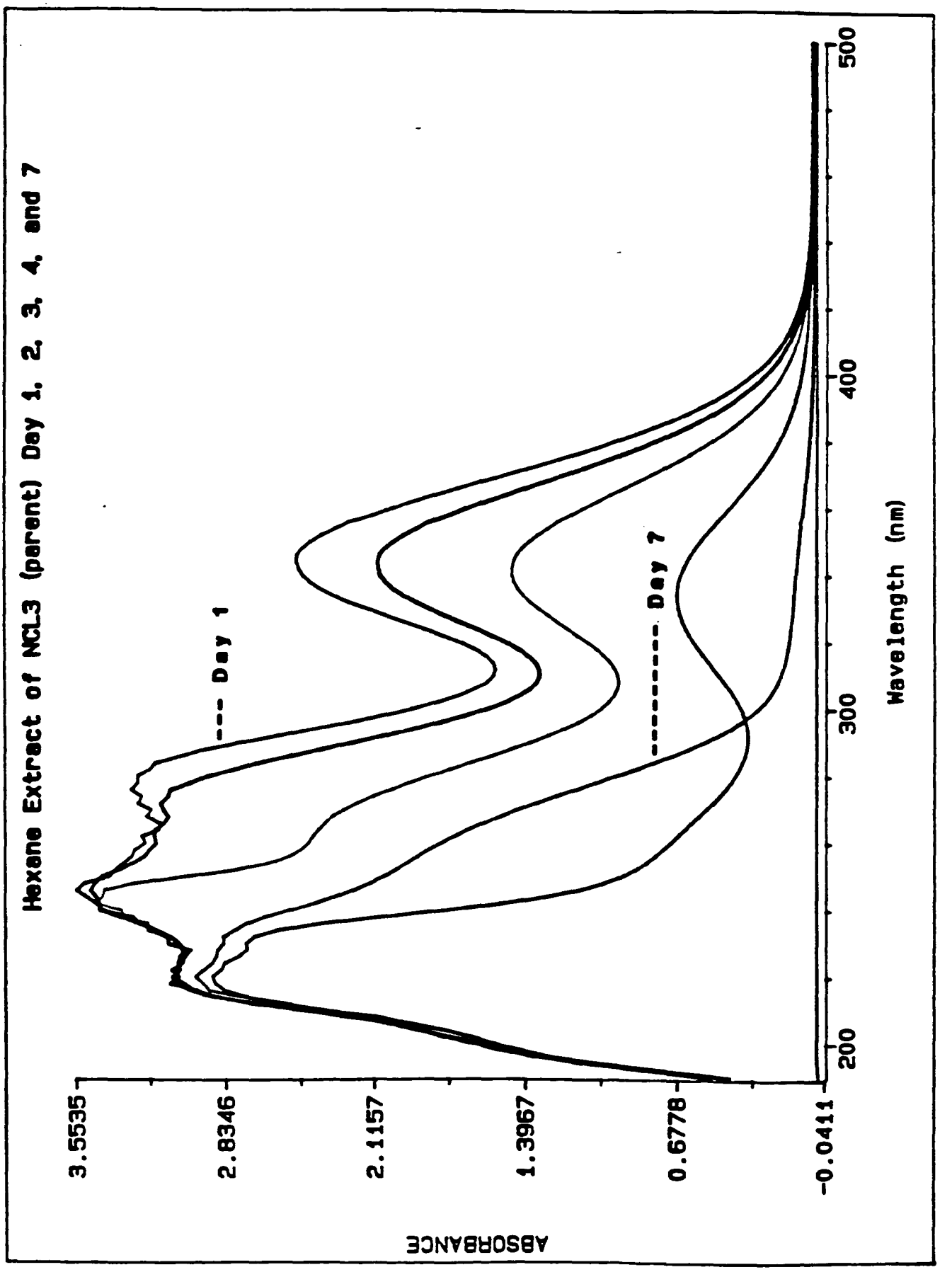

Hexane Extract of NCL3 (parent) Day 1, 2, 3, 4, and 7
--- Day 1
-------- Day 7
ABSORBANCE
3.5535
2.8346
2.1157
1.3967
0.6778
-0.0411
200
300
400
500
Wavelength (nm)

Fig. 10

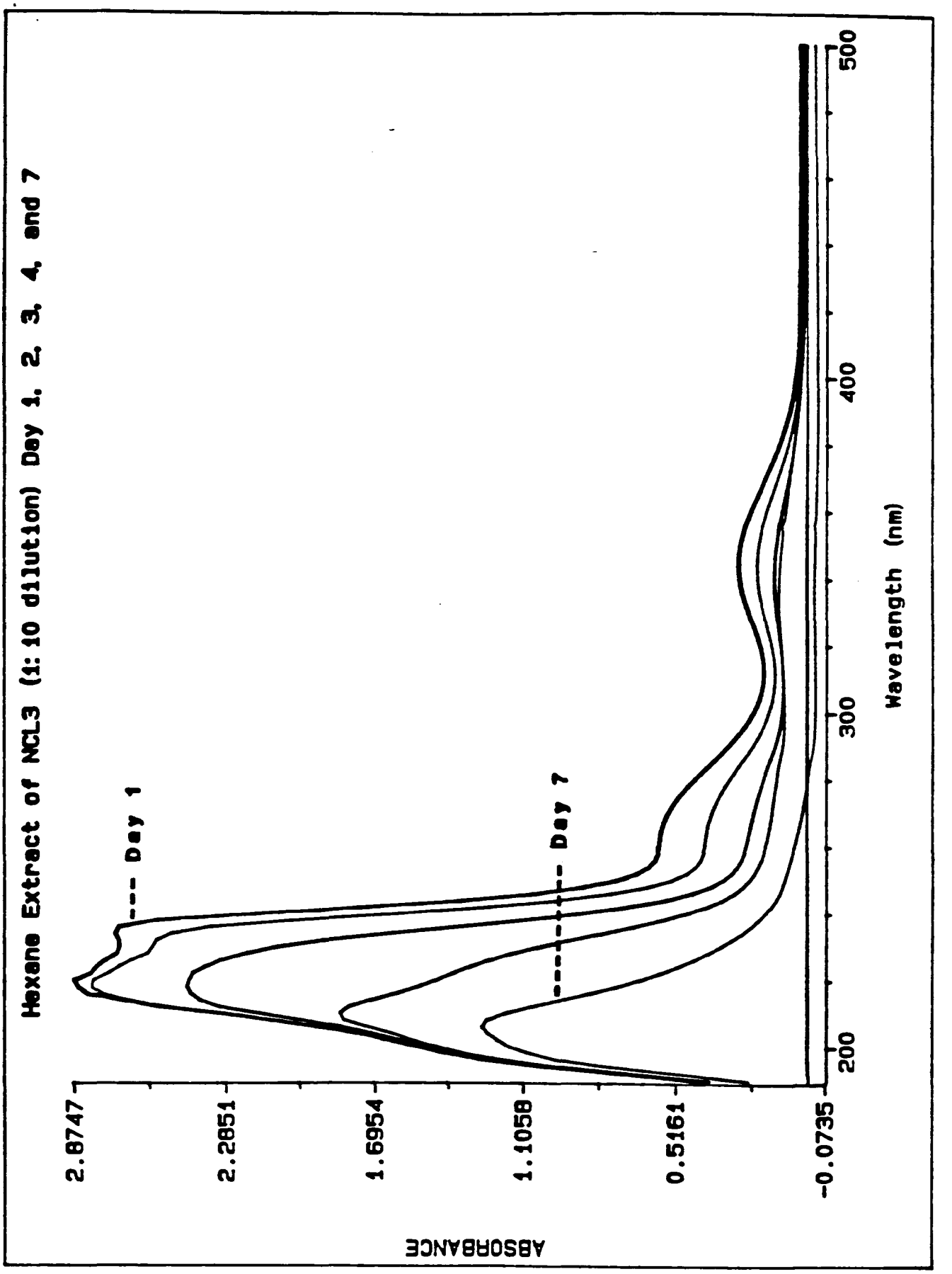

Hexane Extract of NCL3 (1:10 dilution) Day 1, 2, 3, 4, and 7
--- Day 1
---------- Day 7
ABSORBANCE
2.8747
2.2851
1.6954
1.1058
0.5161
-0.0735
200
300
400
500
Wavelength (nm)

Fig. 11

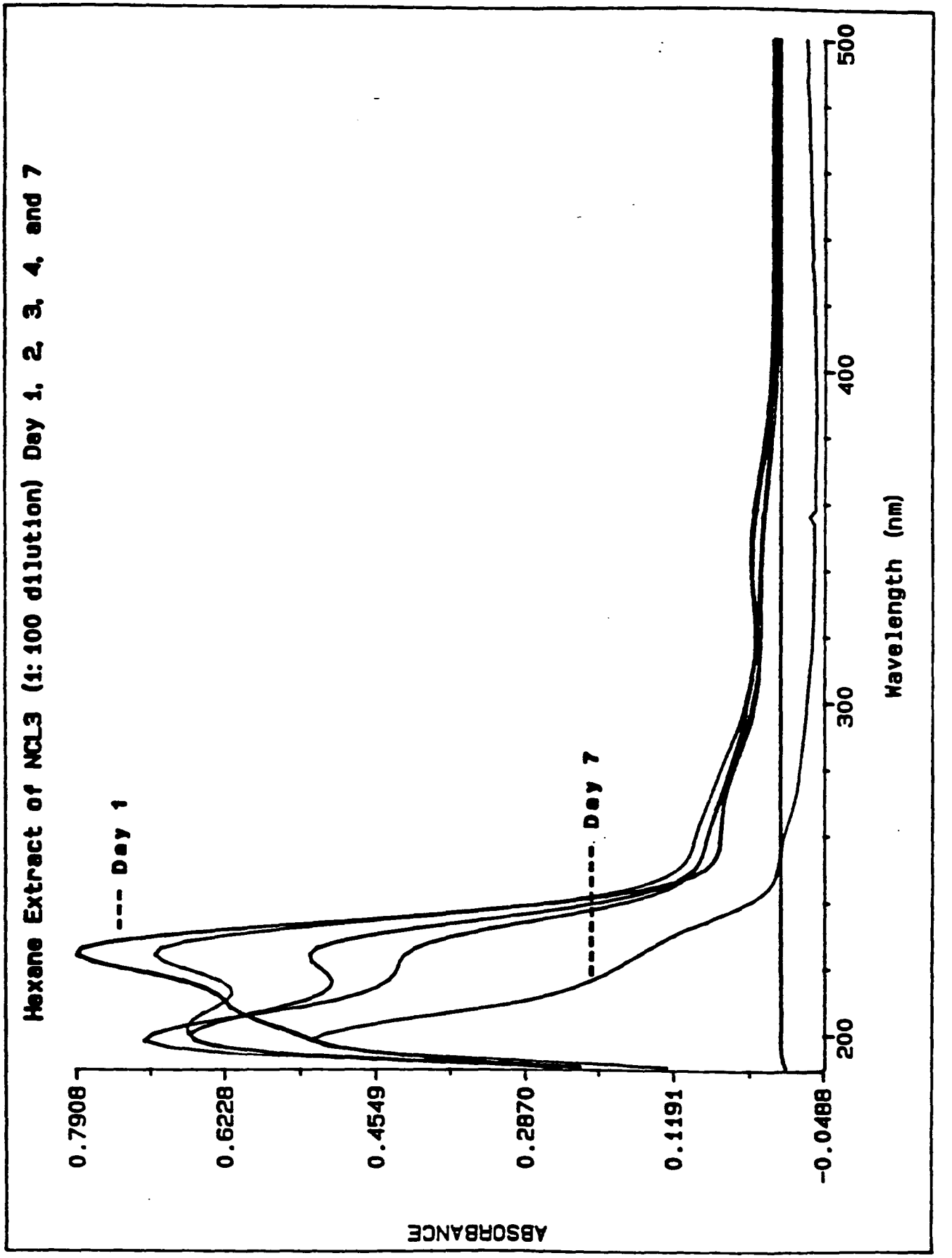

Hexane Extract of NCL3 (1:100 dilution) Day 1, 2, 3, 4, and 7
--- Day 1
---- Day 7
ABSORBANCE
0.7908
0.6228
0.4549
0.2870
0.1191
-0.0488
200
300
400
500
Wavelength (nm)

Fig. 12

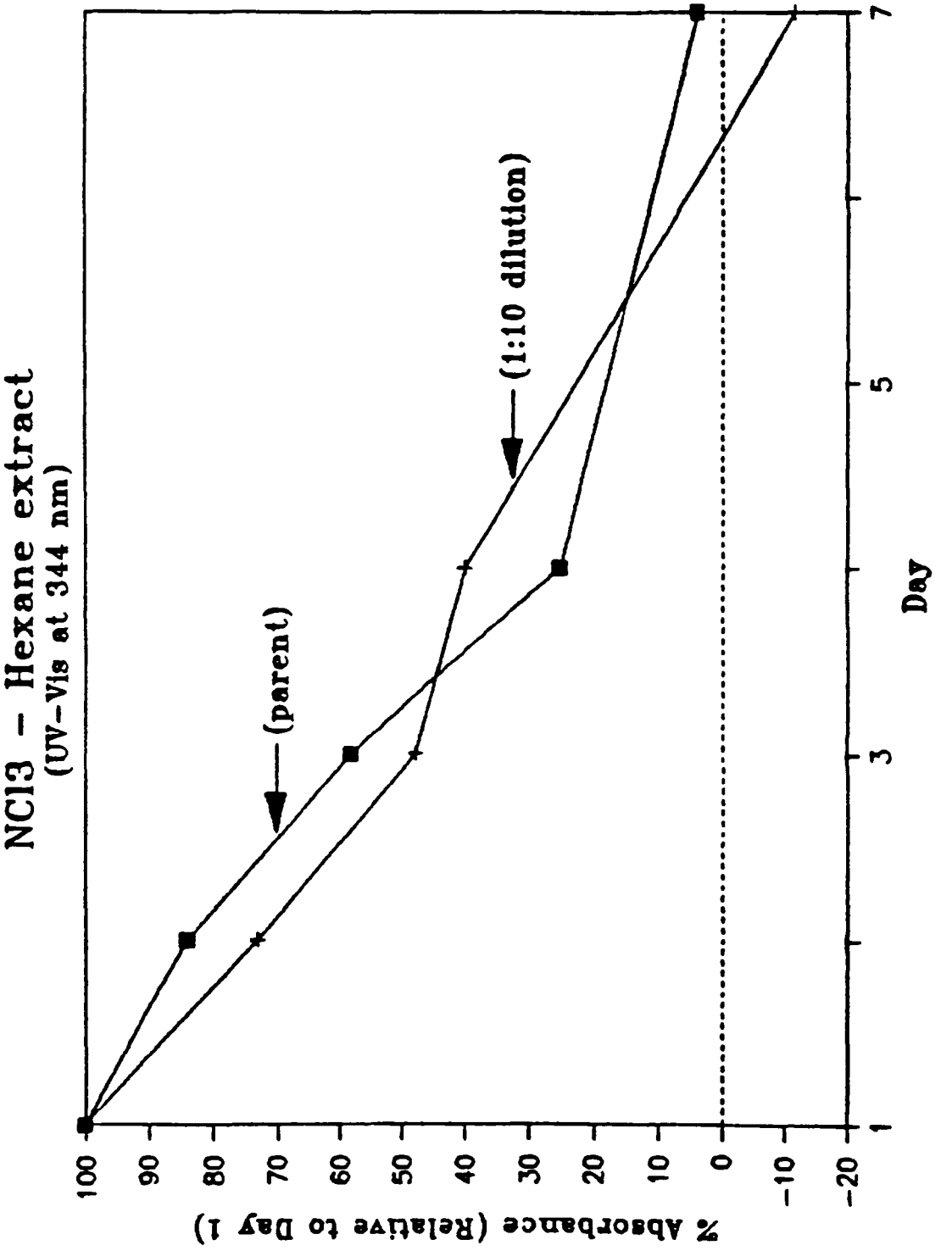

NC13 - Hexane extract
(UV-Vis at 344 nm)
(parent)
(1:10 dilution)
% Absorbance (Relative to Day 1)
100
90
80
70
60
50
40
30
20
10
0
-10
-20
1
3
5
7
Day

Fig. 13

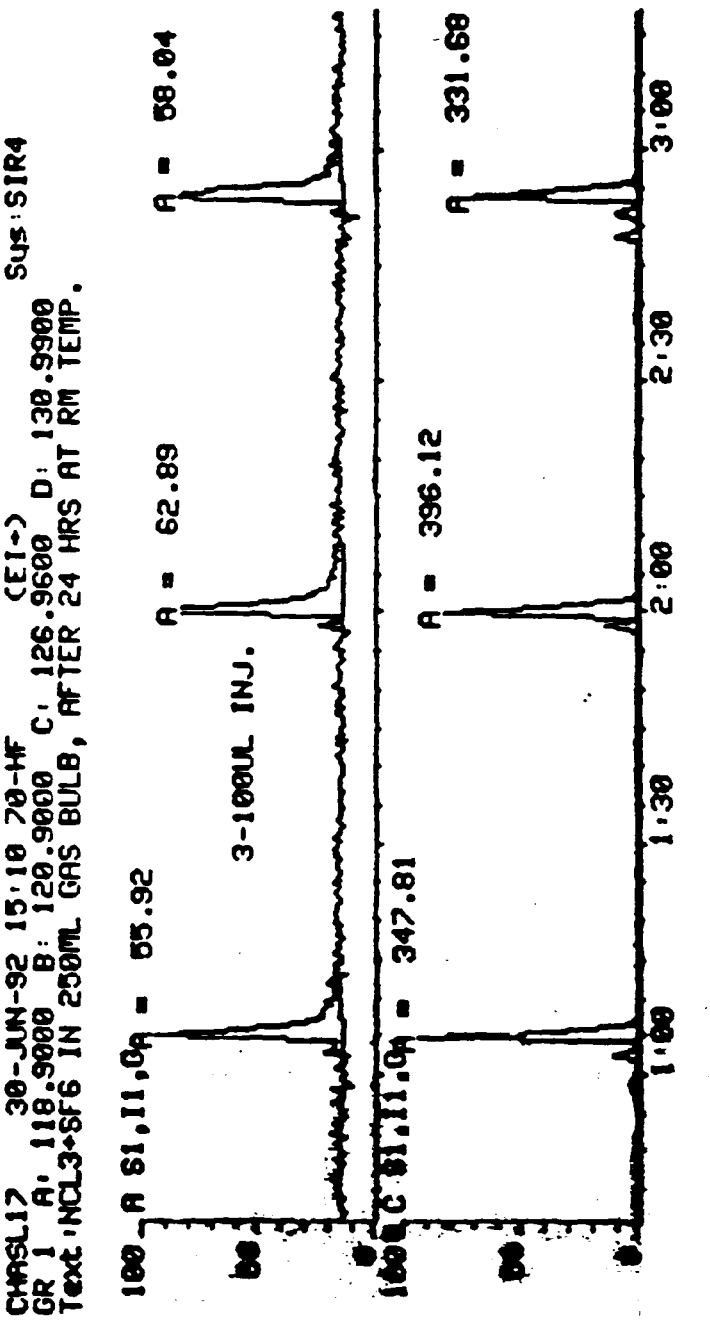

CHASL12 30-JUN-92 15:10 70-HF (EI-) Sys:SIR4
GR 1 A: 118.9000 B: 120.9000 C: 126.9600 D: 130.9900
Text:NCL3+SF6 IN 250ML GAS BULB, AFTER 24 HRS AT RM TEMP.
A 81,11,04 = 55.92
3-100UL INJ.
A = 62.89
A = 68.04
C 81,11,04 = 347.81
A = 396.12
A = 331.68
1:00
1:30
2:00
2:30
3:00

Fig. 14

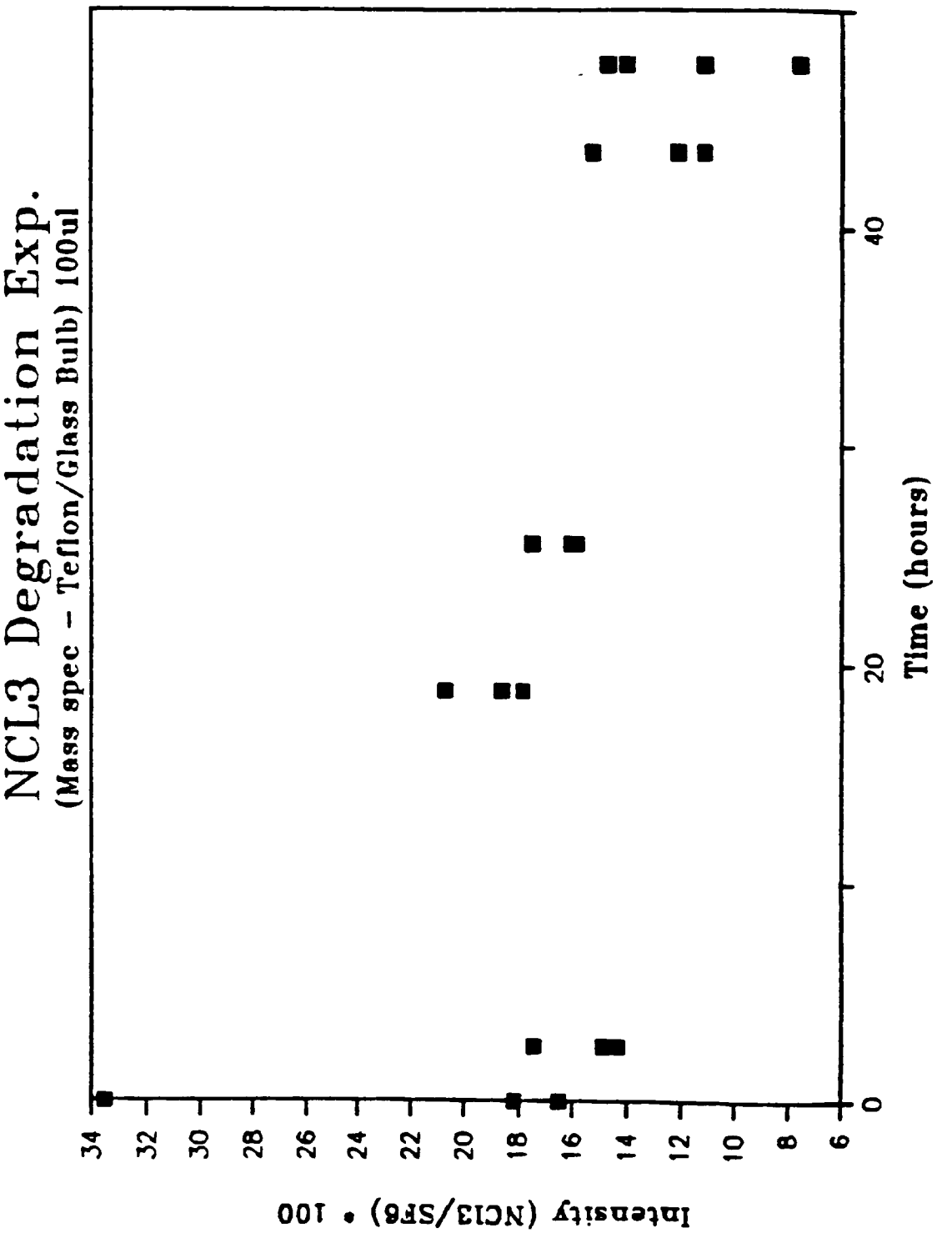

NCL3 Degradation Exp.
(Mass spec - Teflon/Glass Bulb) 100ul
Intensity (NCl3/SF6) * 100
Time (hours)
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
0
20
40

Fig. 15

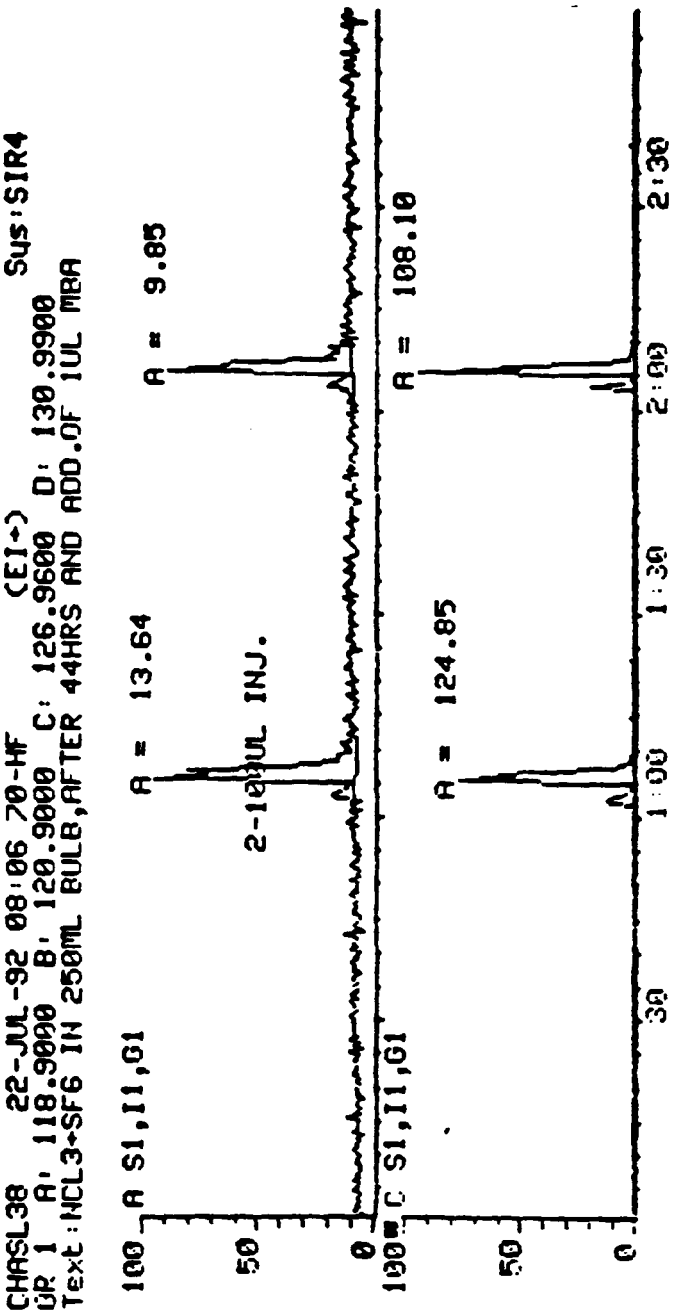

CHASL38 22-JUL-92 08:06 70-HF (EI+) Sys:SIR4
UR 1 A: 118.9000 B: 120.9000 C: 126.9600 D: 130.9900
Text:NCL3+SF6 IN 250ML BULB,AFTER 44HRS AND ADD.OF 1UL MBA
A S1,I1,G1
A = 13.64
A = 9.85
2-10UL INJ.
C S1,I1,G1
A = 124.85
A = 108.10
100
50
0
30
1:00
1:30
2:00
2:30

Fig. 16

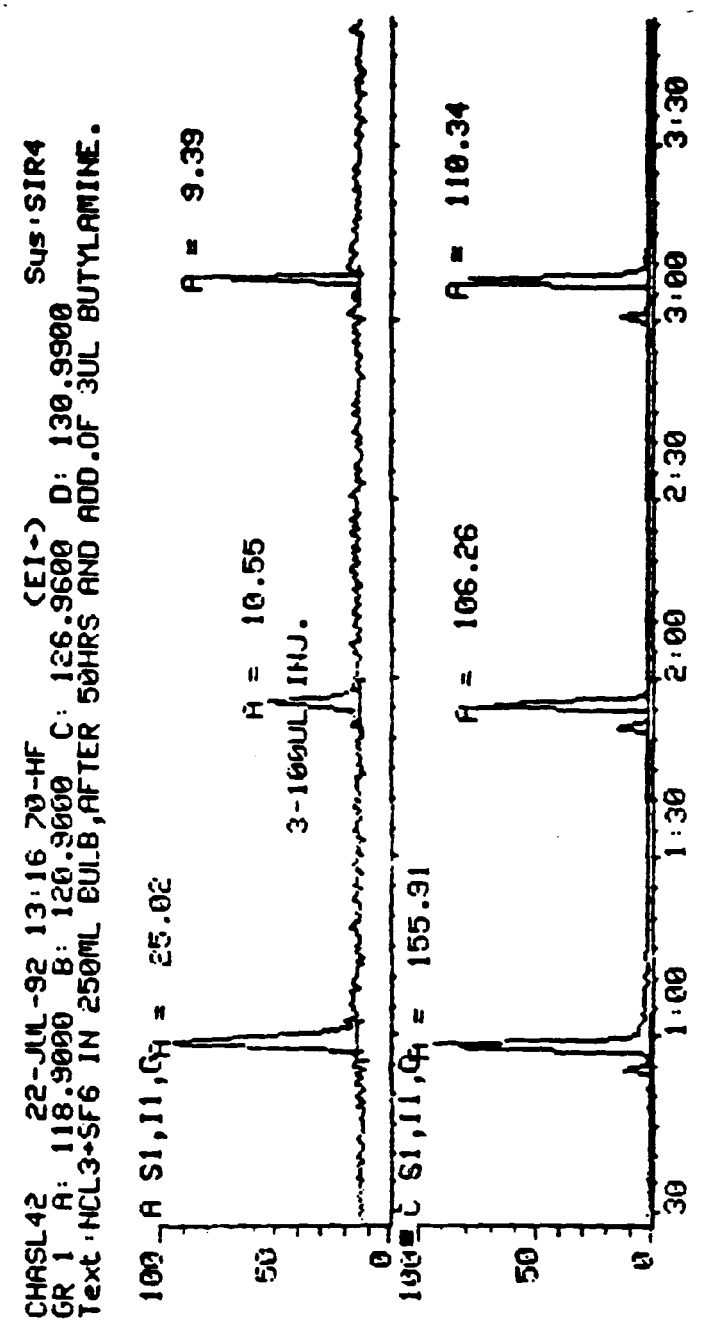
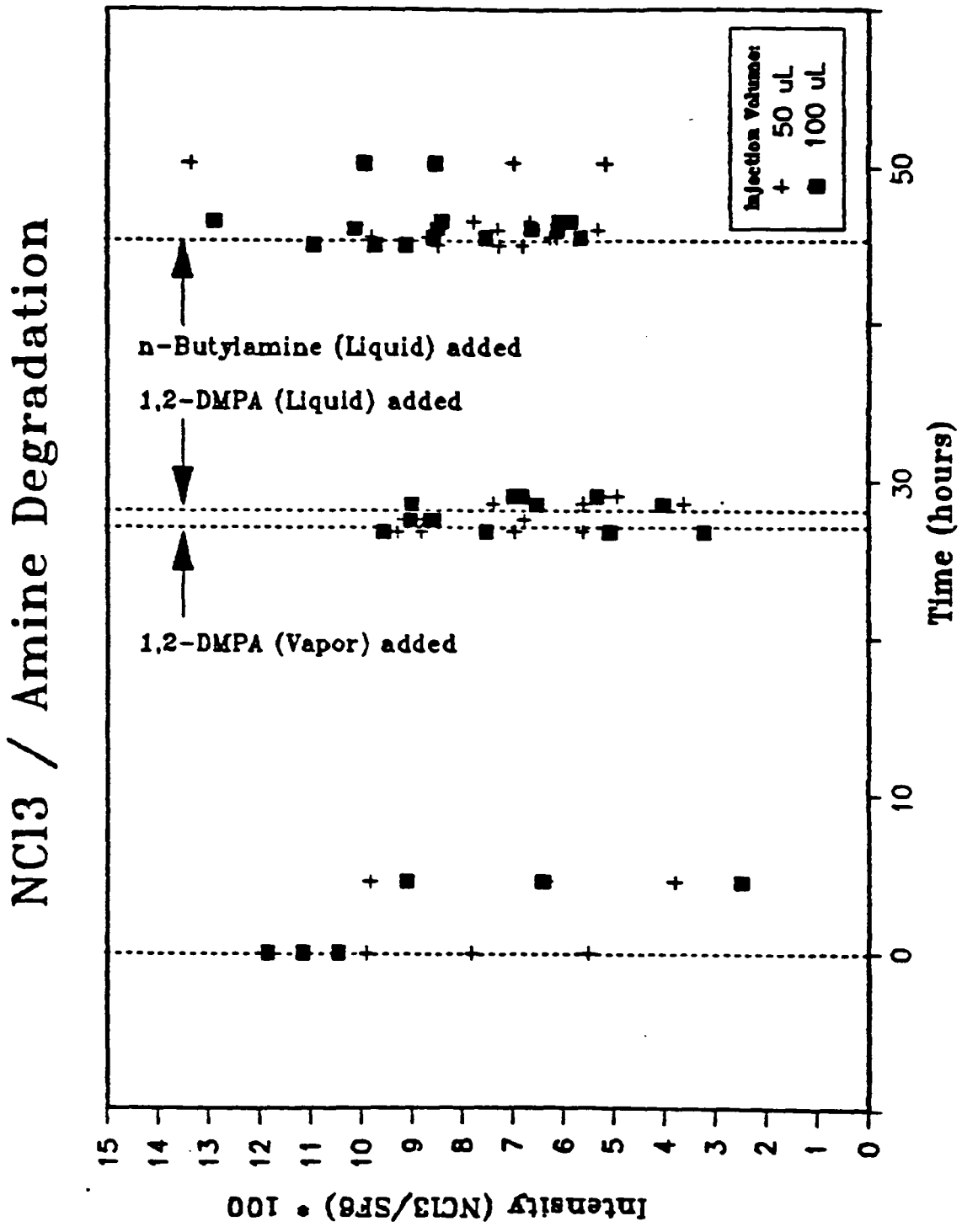

CHASL42 22-JUL-92 13:16 70-HF (EI-) Sys:SIR4
GR 1 A: 118.9000 B: 120.9000 C: 126.9600 D: 130.9900
Text:NCL3-SF6 IN 250ML BULB,AFTER 50HRS AND ADD.OF 3UL BUTYLAMINE.
A S1,11,C4 = 25.02
A = 9.39
A = 10.55
3-100UL INJ.
A = 106.26
A = 110.34
C S1,11,C4 = 155.91
100
50
0
1:00
1:30
2:00
2:30
3:00
3:30

Fig. 17


NCl3 / Amine Degradation
Injection Volume:
50 uL
100 uL
n-Butylamine (Liquid) added
1,2-DMPA (Liquid) added
1,2-DMPA (Vapor) added
Time (hours)
0
10
30
50
Intensity (NCl3/SF6) * 100
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15