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Waste Tank Organic Safety Program

Analytical Methods Development: FY 1994 Progress Report

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Abstract

This report describes the FY 1994 progress obtained by Pacific Northwest Laboratory in developing the strategy and tools for the analysis of Hanford waste tanks for organic constituents. The project also has engaged in analysis of actual waste samples by newly developed techniques, and where appropriate, transfers developed technology to other laboratories for routine applications to tank waste samples.

A letter report discussing total organic carbon (TOC) accountability was submitted during FY 1994. A criterion for TOC accountability was developed. In those instances in which speciation is not required, functional group analysis using Raman spectroscopy may provide sufficient data. Preliminary results indicate that functional groups can be identified without speciation.

Among the state-of-the-art techniques explored for more efficient analysis of organics in tank waste were electrospray mass spectrometry (MS), supercritical fluid extraction (SFE), and capillary electrophoresis (CE). Electrospray MS is a technique for the direct analysis of water-soluble organics, and was evaluated for the analysis of chelators and chelator fragments. The base ion in negative ion electrospray MS was $(M-H)^-$ in most cases. Development of separation procedures is being initiated. Preliminary studies were performed to determine the feasibility of extracting derivatized chelators from a complex matrix using SFE. Results indicate that derivatized ethylenediaminetetraacetic acid (EDTA) and lauric acid could be effectively recovered from sand using supercritical fluid carbon dioxide. Capillary electrophoresis was also evaluated for the separation of chelators and chelator fragments. Preliminary results indicate that chelators such as nitrilotriacetic acid (NTA) and EDTA can be separated.

High resolution mass spectrometry (HRMS) was used to identify derivatized components in samples from Tank 101-SY and the organic layer from Tank C-103. The recently acquired tandem JEOL mass spectrometer has been utilized for analytical methods development, primarily with electrospray ionization.

The use of cation exchange resins for the reduction of radioactivity in tank waste samples permits removal waste samples from the hot cell prior to derivatization. This technique made a substantial contribution to the ability to account for most of the organic carbon in samples from Tank 101-SY. High temperature extraction were performed in an attempt to increase the amount of water-soluble carbon leached from tank waste samples. These experiments were unsuccessful in that abundant gas was generated; in view of the fact that enhanced recoveries were realized by the resin separation technique, no further investigations were conducted.

Several analytical methods developed for the analysis of chelators and chelator fragments using derivatization gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS) were transferred to personnel in the 222-S laboratory and the Analytical Chemistry Laboratory (ACL). In addition, methods for the analysis of N-(2-hydroxyethyl) ethylenediaminediacetic acid (HEDTA), EDTA, and low molecular weight acids (LMWA) were also transferred to the 222-S laboratory.

A suite of chemical analyses were performed in support of activities directed toward the resolution of an Unreviewed Safety Question (USQ) concerning the potential for a floating organic layer in waste Tank C-103 to sustain a pool fire.

Capital equipment acquisitions in FY 1994 included a Raman spectrometer, a CE instrument, and an array detector for the high resolution mass spectrometer. Both the Raman and CE instruments were delivered in FY 1994. The array detector is still in the development stage.

Summary

This report describes the status of developing analytical methods to account for the organic constituents in Hanford waste tanks, with particular emphasis on those tanks that have been assigned to the Organics Tanks Watch List. The methods developed were applied to the analysis of samples from Tanks C-103 and T-111.

A derivatization GC/MS method analyzing chelators, chelator fragments , and carboxylic acids, and an LC/MS method for the identification of LWMA have been transferred to personnel in the Analytical Chemistry Laboratory (ACL) and the 222-S laboratory. Although developed primarily under the Flammable Gas Safety Program, refinements were made under the Organic Tanks Safety Program, and the methods were transferred under the auspices of that program.

The ratio of carbon identified by speciation to the carbon analyzed as TOC is defined as the TOC accountability. A criterion for TOC accountability was proposed. In a letter report presented during FY 1994 (Campbell et al. 1994), the level of TOC accountability required was deemed to be dictated by the objective for the data. As an example, the analytical data obtained from analyses of samples from Tank C-103 was utilized to answer a USQ; organic speciation was required. However, in instances where the data is used to answer energy considerations, functional group analysis without organic speciation may be sufficient. In general, for those cases in which a safety question is addressed, organic speciation will be required. The desired objective is to have 100% TOC accountability; a more realistic level may be 80 to 90%.

In those cases in which speciation is not required for the data objective, functional group analysis may provide sufficient information. Raman spectroscopy has been evaluated for functional group analysis as a potential substitute for TOC accountability (Campbell and Lerner 1994). The important functional groups that have thus far been identified in tank waste include carboxylates, nitrous, hydrocarbons, phosphates, alcohols, amines, ketones, and nitriles. The priority of the functional groups will be evaluated on a case-by-case basis. Standards of chelators, chelator fragments, and carboxylic acids were analyzed by Raman spectroscopy. Preliminary results indicate that functional groups can be identified without speciation. The next step is to analyze simulated wastes and then proceed to actual waste samples.

Electrospray MS has the potential of analyzing the water-soluble organics directly. In view of the fact that many of the tanks under the Organics Tanks Safety Program contain chelators and chelator fragments, a logical application is for the analysis of chelators and chelator fragments. Derivatization GC/MS has been the method of choice for the analysis of chelators. However, the lack of volatility and polarity of the chelators and chelator fragments preclude direct analysis by GC/MS. The method of choice has been the formation of methyl esters by the reaction of boron trifluoride (BF_3)/methanol. This procedure requires a completely dry sample to ensure high conversion to the methyl esters and is very time- consuming; Thus, work is continuing on utilizing electrospray MS to analyze chelators and chelator fragments; this method requires no derivatization. Additional work has been initiated to develop a separation scheme for a mixture of chelators and chelator fragments. The results will be applicable to both the Flammable Gas Safety and Organics Tanks Safety Programs.

Separation by electrophoresis is obtained by differential migration of solutes in an electric field using narrow-bore capillaries. Capillary electrophoresis (CE) has the potential for the direct separation and identification of components in waste, without derivatization. This technique was applied to the separation of chelators and organic acids. Preliminary results indicate that chelators, e.g., NTA and EDTA could be separated. In addition, the separation of metal complexes was also investigated. The results will have implications for the Flammable Gas Safety Program and the Organics Tanks Safety Program.

Supercritical fluid extraction has been used to extract nonpolar organics from complex matrices. In addition, SFE has the potential of separating the radioactive components from the organics and minimizing waste production. A SFE instrument was purchased during FY 1994. The feasibility of extracting derivatized chelators from a complex matrix using SFE was studied. Results indicate that derivatized EDTA and lauric acid could be effectively recovered from sand, a test matrix, using supercritical fluid carbon dioxide. If successful, SFE would separate the radioactive components and increase the lifetime of the derivatives. Currently, the lifetime of the methyl-ester derivatives, as analyzed by derivatization GC/MS, is approximately 24 hours; the methyl esters tend to hydrolyze to the carboxylates after that time.

High resolution mass spectrometry (HRMS) has provided an invaluable tool for analysis of tank waste. This technique has been utilized to identify derivatized components in waste from Tank 101-SY and unknown organic components in the organic layer from Tank C-103. The HRMS instrument continues to provide a valuable resource for methods development.

Samples from the organic and aqueous layers of Waste Tank 241-C-103 (Tank C-103) were analyzed using GC/MS. The work was performed as part of a larger work-ordered project to investigate the organic and inorganic composition of Tank C-103 organic layer and underlying aqueous phase. The work is reported here to illustrate the applicability of the methods development task to practical Waste Tank Safety problems. The organic layer, aqueous layer, and headspace above both the organic and aqueous layer were analyzed for organics. Samples from Tank T-111 were analyzed for organics.

Glossary

ACL	Analytical Chemistry Laboratory
CA	citric acid
CE	capillary electrophoresis
DBBP	dibutylbutyl phosphonate
ED3	Aethylenediaminetriacetic acid
EDTA	ethylenediaminetetraacetic acid
ESI	electrospray ionization
FID	flame ionization detector
FTIR	Fourier transform infrared
GC/MS	gas chromatography/mass spectrometry
HEDTA	N-(2-hydroxyethyl) ethylenediaminetriacetic acid
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
IDA	iminodiacetic acid
LC	liquid chromatography
LC/MS	liquid chromatography/mass spectrometry
LMWA	low molecular weight acids
NED3A	N-nitrosoethylenediaminetriacetic acid
NIDA	nitrosoiminodiacetic acid
NTA	nitrilotriacetic acid
NPH	normal paraffin hydrocarbon
PEG	polyethylene glycol
PFK	perfluorokerosene
SA	succinic acid
SEM	scanning electron microscopy
SFE	supercritical fluid extraction
SIM	selected ion monitoring
SWM	simulated waste material
Tank 241-SY-101	Tank 101-SY
Tank 241-C-103	Tank C-103
TBP	tributyl phosphate
TOC	total organic carbon
UV	ultraviolet
USQ	Unreviewed Safety Question
WHC	Westinghouse Hanford Company

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1.0 Introduction

The objectives of this task are to develop and document extraction and analysis methods for organics in waste tanks, and to extend these methods to the analysis of actual core samples to support the Waste Tank Organic Safety Program. This report documents progress at Pacific Northwest Laboratory[(a)] during FY 1994 on methods development, the analysis of waste from Tanks 241-C-103 (Tank C-103) and T-111, and the transfer of documented, developed analytical methods to personnel in the Analytical Chemistry Laboratory (ACL) and 222-S laboratory. This report is intended as an annual report, not a completed work.

The ratio of carbon identified by speciation to the carbon analyzed as total organic carbon (TOC) is defined as TOC accountability. Efforts were undertaken to develop a criterion for TOC accountability, the level dictated by the objective for the data (Campbell et al. 1994). As an example, if the analytical work is required to provide data to address an Unreviewed Safety Question (USQ), the required level of TOC accountability may be different in instances where the data is used to address energetics. In other instances, functional group analysis may be sufficient to answer the specific question and provide a substitute for speciation.

Methods currently used to analyze tank waste samples for organics include derivatization gas chromatography/mass spectrometry (GC/MS), liquid chromatography (LC), and liquid chromatography/mass spectrometry (LC/MS) (Campbell et al. 1994). While these analysis techniques provide valuable information of the organic components in the waste samples, they, in general, are time-consuming, generate a substantial amount of additional waste, and can introduce interferences or artifacts due to the derivatization GC/MS procedures. In order to address these limitations, methods development during FY 1994 has focused on identifying and testing alternative analytical methods that may provide the desired results of organic analysis more effectively. The techniques being tested for their application to organic analysis of complex matrices are the following: Raman spectroscopy, electrospray ionization (ESI), capillary electrophoresis (CE), and supercritical fluid extraction (SFE).

Derivatization GC/MS and LC/MS have been utilized to analyze water-soluble organics. Derivatization GC/MS is time-consuming and labor-intensive, recoveries may vary, most derivatizing reagents are toxic, and the derivatives are stable for only a limited period of time. In view of these limitations, efforts are underway to develop alternatives for the analysis of chelators and low molecular weight carboxylic acids (LMWA). Electrospray MS is a technique for analyzing aqueous leachates of tank waste directly.

Separation by electrophoresis is obtained by differential migration of solutes in an electric field using narrow-bore capillaries. Capillary electrophoresis has the potential for the direct separation and identification of components in waste, without derivatization. Efforts were initiated to apply CE to the separation of chelators and organic acids. In addition, efforts were also undertaken for the separation of metal complexes. The results will have implications for the Flammable Gas Safety Program and the Organics Tanks Safety Program.

(a) Pacific Northwest Laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute.

In order to minimize the amount of waste produced during the derivatization GC/MS procedure and increase the lifetime of derivatives, the application of supercritical fluids for extracting derivatized chelators was also initiated. If successful with actual wastes, the radioactive constituents would be isolated, and the lifetime of the derivatives may be longer than the current lifetime of only 24 hours.

Studies of simulated waste under Waste Aging, Concentration Mechanisms, and Energetics tasks were undertaken during FY 1994. Analytical support was provided to determine the extent of degradation and identify degradation components. Methods development was required to determine several of the analytes.

This report describes the progress made in FY 1994 in developing more effective procedures for separating and preparing samples, for isolating and derivatizing components, and for identifying components. In addition, several methods developed during this work either have been transferred or are in the process of being transferred to other laboratories for routine applications.

2.0 Summary of Results

The ratio of carbon identified by speciation to the carbon analyzed as total organic carbon (TOC) will be defined as the TOC accountability. Detailed organic speciation will be required in instances where the data is required to address tanks containing a floating organic layer, entrained organic layer, nitrite - nitrate organic reactors, and flammable gases as described in Data Quality objective (DQO) and test plans. The natural objective is to have 100% TOC accountability, but that may be an unrealistic expectation; a more realistic level may be 80-90% TOC accountability. At that point, the cost to account for the rest of the TOC must be weighed with the value of the additional speciation information. That judgment must be made on a case-by-case basis by DQO or test plan authors. After the level of TOC accountability is determined, a decision can then be made as to the necessity for additional definitive organic analyses. If the TOC accountability is poor, much more effort may be required to determine the identity of actual organic materials present in the waste matrix. For those cases in which the data is strictly used for energetics considerations and calculation of heat release, a 60% TOC accountability may be sufficient. Functional group analysis coupled with molecular weight distribution data or compound class identification for the rest of the TOC may also be required.

Situations may also arise in which only functional group analysis may be required to fully address the particular concern or data objective. In those instances, functional group analysis will be performed using Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). Raman spectroscopy has been evaluated for functional group analysis as a potential substitute for TOC accountability (Campbell and Lerner 1994). Preliminary results indicate that functional groups can be identified without speciation. The important functional groups that have thus far been identified in tank waste include carboxylates, nitroso, hydrocarbons, phosphates, alcohols, amines, ketones, and nitriles. The priority of the functional groups will be evaluated on a case-by-case basis although no DQO has yet requested functional group analysis; pretreatment might possibly consider this technique. Standards of chelators, chelator fragments, and carboxylic acids were analyzed by Raman spectroscopy. The next step is to analyze simulated wastes and then proceed to actual waste samples.

Derivatization GC/MS has been utilized to analyze chelators, chelator fragments, and carboxylic acids in waste. Although this procedure provides satisfactory results, it is time-consuming, requiring 3 to 5 d to complete, and labor-intensive. In addition, unless the sample is completely dry, variable recoveries may be obtained. Often, the derivatizing reagent is extremely toxic and the derivatives produced usually have a lifetime of only 24 h. As a result, direct analysis methods not requiring derivatization are being evaluated. Electrospray ionization is a relatively new ionization method recently acquired on the JEOL SX-102/SX-102 high resolution tandem mass spectrometer. Electrospray MS is an effective method of analyzing nonvolatile analytes in solution without prior derivatization. The negative ion ESI spectrum of ethylenediaminetetraacetic acid (EDTA) shows both the singly and doubly charged ions. The singly charged species, $(M-H)^-$, is the predominant peak for N-(2-hydroxyethyl) ethylenediaminetriacetic acid (HEDTA). Intact metal chelates have also been studied using ESI; Fe-EDTA. A mixture of $Fe(NO_3)_2$ and the sodium form of EDTA were mixed. In the ESI spectrum, the NO_3^- counter was the base ion, but the other ions of interest, indicative of the intact complex, were still observed at higher m/z.

The feasibility of utilizing SFE with in situ derivatization was examined. A sample consisting of sand spiked with EDTA and lauric acid was derivatized with boron trifluoride (BF_3)/methanol to form

the methyl esters, then extracted with supercritical fluid carbon dioxide (CO_2). Preliminary results indicate that both compounds could be quantitatively recovered using SFE. The lifetime of the methyl ester derivatives is approximately 24 h; the tendency is for the derivatives to hydrolyze back to the carboxylates. If successful with actual waste, use of SFE might segregate the radioactive components and increase the lifetime of the derivatives. Other analytes that may be extracted by SFE include normal paraffin hydrocarbon (NPH) and tributyl phosphate (TBP).

Separation by electrophoresis is obtained by differential migration of solutes in an electric field. In CE, electrophoresis is performed in narrow-bore capillaries, typically 25- to 75-μm inner diameter. Preliminary results indicate that chelators, e.g., nitrilotriacetic acid(NTA) and EDTA, can be separated using CE. In addition, metal complexes such as Sr- and Fe-EDTA complexes were separated. Additional peaks were also observed, probably due to mixed-metal complex interactions. Further studies are underway. Other analytes that may be separated and analyzed by CE include amines, phosphates, and small and large organic acids.

The high resolution mass spectrometer has been used to identify components in the derivatization GC/MS total ion chromatogram of waste from Tank 101-SY. In addition, components in samples of the organic layer from Tank C-103 were unambiguously identified (Pool et al. 1994). This instrument has helped solve problems associated with tank waste, and has made a significant contribution in analytical methods development.

The results of high temperature extraction of waste samples from Tank 101-SY were discussed in a letter report. Campbell 1994, high temperature extraction did not increase the amount of water-soluble organic carbon; the convective layer samples produced large amounts of gas during heating. Continuous or repetitive extractions was suggested to increase the water-soluble organic carbon for cases in which the TOC accountability is low.

A suite of chemical analyses were performed in support of activities directed toward resolving an USQ concerning the potential for a floating organic layer in waste Tank C-103 to sustain a pool fire. The composition of the organic layer was primarily TBP and NPH. The relative weight ratio of TBP:NPH was 67:33, if dibutyl butyl phosphonate (DBBP) was included with TBP and the branched alkanes were included with NPH (Pool et al. 1994). Tributyl phosphate constituted 48.3% by volume of the organic layer, and the primary constituents in the aqueous layer were TBP and DBBP. The analytical results were instrumental in resolving the USQ. In addition, the headspace vapors above the aqueous layer and organic layer were analyzed using GC/flame ionization detector (FID) and GC/MS. Primary components identified in the headspace vapors above the organic layer include ketones, alkanes, and nitriles. In addition, a sample from Tank T-111 was analyzed for organics. In this instance, $< 10\%$ of the TOC could be accounted for. Further efforts are planned in FY 1995 to resolve this problem.

Methods developed by the Advanced Organic Analytical Methods Group have been transferred to personnel in both the ACL and the 222-S laboratory. A method involving derivatization GC/MS for analyzing chelators, chelator fragments, and carboxylic acids, and an LC/MS method for the analysis of LWMA have been transferred; etter of transfer were signed on May 7, 1994, by Kim Wehner of the 222-S laboratory and May 24, 1994 by Robert Stromatt of the ACL to acknowledge receipt. Additional training and consultation will be available if required. Both methods were primarily developed under the Flammable Gas Safety Program and transferred under the auspices of the Organic Tanks Safety Program.

3.0 Discussion of Methods

3.1 Total Organic Carbon Accountability

Total organic carbon is typically determined using persulfate oxidation or combustion. Both of these methods rely on several assumptions to yield their TOC results. The persulfate oxidation assumes three things: that oxidation of organics will not occur when the sample is added to an acidic solution to release inorganic carbon (carbonate or bicarbonate) as CO_2, volatile organics are not lost when the sample is added to the acid solution nor when the solution is heated, and all organics are oxidized by the silver and heat catalyzed persulfate oxidation of the organic carbon to CO_2. The combustion method assumes that all organics will be oxidized at 600° C to CO_2, and inorganic carbonate species will not decompose at that temperature.

The TOC analysis by either combustion or persulfate oxidation does not provide data about the types of organic species present in the waste; the analyses merely provide a determination of the total amount of organic carbon in the sample. While this data is important in determining general risk associated with organics in tank waste, it is not sufficient for a full assessment of the hazards associated with the organics. This discussion will attempt to outline a detailed analysis for organic speciation (concentration and identification), where required, in order to better understand the risks related to tank waste.

Detailed analysis to provide speciation of the organics is performed using gas chromatography/ mass spectrometry (GC/MS), liquid chromatography (LC), LC/MS, high resolution mass spectrometry (HRMS), and other techniques. Each organic component contributes to TOC. Ethylenediaminetetraacetic is an example of a major component present in the waste. The molecular formula for EDTA is $C_{10}H_{16}O_8N_2$; the percent carbon in EDTA is 41% (number of carbons X wt of carbon/molecular weight of EDTA =120/292). From the concentration of EDTA in the sample, the amount of carbon associated with EDTA can be determined. This procedure can be extended to all the identified organics. The summation of all the carbon identified through detailed analysis is then compared to the TOC value. This ratio of carbon identified by speciation to the TOC will be defined as the "TOC accountability". Once the level of TOC accountability is determined, a decision can then be made as to the necessity for additional definitive organic analyses. If the TOC accountability is poor, much more effort may be required to determine the actual organic materials present in the waste matrix.

The level of TOC accountability required is dictated by the proposed use for the data. For example, if the analytical work is required to provide data for a Safety Analysis Report (SAR) that addresses a USQ, the required level of TOC accountability by detailed analysis may be different in the case where the data is used to support proposed mechanisms for production of flammable gases. In addition, the requirements will be different in cases where the analytical work provides only information for energetics considerations. The TOC determination alone may not suffice to answer some these issues. However, determination of the TOC provides a sensitive measure of carbon content but can't be used to identify particular risks associated with certain organics. Examples are discussed which illustrate the reason for organic speciation in specific tank wastes.

Tank C-103 contains a floating organic layer with an underlying aqueous layer. The possibility exists that a pool fire might occur in the organic layer that would result in a loss of containment and potential radiation release to the surrounding environment. The primary purpose of the analytical data obtained from C-103 was to provide information for a safety analysis on the potential for the combustion of the organic layer. In addition, there is circumstantial evidence that indicates organic chemical releases from Tank 103-C may be responsible for adverse health effects on some tank farm workers. As a result, the flash point of the organic layer was measured, composition of the organic layer was determined, and the vapor composition above the organic layer at three different temperatures was also determined. Composition information was required for calculations to estimate the lower flammability limit (LFL) of the organic layer.

The principal constituents in the organic layer from Tank C-103 were found to be normal paraffin hydrocarbon (NPH) and tributyl phosphate (TBP). Branched alkanes and dibutylbutyl phosphorate (DBBP) were also found in lower concentrations. The organic composition was determined using GC/MS, only organics of sufficient volatility would be detected. Results show that approximately 25% of a weighed sample could not be accounted for by GC/MS analysis. However, no polymeric material or high molecular organic residues were observed. Analysis using scanning electron microscopy (SEM) indicated a portion of this material consisted of several inorganic phases that would not contribute to the ignition of the organic layer. Analysis of the vapor over the organic liquid heated to 40, 70, and 100°C showed the major components were NPH and NPH-related at all temperatures. Characterization of the aqueous layer was also considered important to resolving the USQ, although not as critical as the analysis of the organic layer. Extracts of the aqueous layer were analyzed using GC/MS; TBP, NPH, and DBBP were present at the μg/mL level. The results of analysis of the vapor above the aqueous layer at several temperatures showed that NPH and TBP were the major components (Pool et al., 1994).

Data from speciation studies of C-103 samples indicate gases and vapors in the headspace of the tank are well below LFL (Huckaby, 1994). The principal fuels in the headspace include low concentration of hydrogen, NPH, and lesser amounts of volatile organic vapors. The flammability of the headspace was estimated to be between 5.5 and 8.4% of the LFL of the mixture. The potential and consequences of a pool fire were discussed in a separate report. In the case of Tank C-103, the organic layer and headspace were not amenable to TOC analysis; the use of organic speciation methods was necessary for the determination of organic components in these phases.

Knowledge of the organic composition may provide insight into the mechanisms involved in the formation of flammable gas mixtures in Tank 101-SY and similar waste tanks. Speciation of the organics may provide a "fingerprint" that might be recognizable in other tanks. Campbell et al. (1994) utilized derivatization GC/MS, LC, and LC/MS to identify chelators, chelator fragments, and low molecular weight acids (LMWA) in samples from Tank 101-SY. The major components detected were EDTA, nitroso-iminodiacetic acid (NIDA), nitrilotriacetic acid (NTA), citric acid (CA), succinic acid (SA), and ethylenediaminetriacetic acid (ED3A). The chelator of highest concentration was EDTA in all six samples analyzed. The amount of organic carbon accounted for by derivatization GC/MS varied from 20 to 52% of the TOC depending on the sample. Preliminary results indicated the chelators and chelator fragments constitute more of the organic carbon in the lower, settled convective than the overlaying nonconvective layer. Liquid chromatography was used to quantitate LMWA (oxalic, formic, glycolic, and acetic acids, which are present in the waste as acid salts); approximately 23 to 61% of the TOC was accounted for by these acids. Oxalic acid constituted approximately 40% of the TOC in the nonconvective layer samples. The reproducibility for the LC determination of oxalic acid

was approximately 5%. The concentration of oxalate in the nonconvective layer was approximately 3 to 4 times higher than the convective layer, a result predicted from solubility concentration. The nonconvective layer sample from the lowest layer analyzed had the highest percentage of water-soluble organic carbon in the form of LMWA. The percent of organic carbon accounted for by all the species identified varied from 73-93%, depending on the depth of the sample. The improved recovery was also a function of when the assay was performed.

The results from 101-SY speciation studies are extremely important to the understanding and support of proposed mechanisms for the production of flammable gases. Knowledge of the organics has had a direct influence on the determination of the mix of organic compounds that should be used in simulated wastes to study gas formation. It also supported assessments of risk of secondary ignition of organic-containing crusts. An important factor in determining the relative yields of nitrous oxide, hydrogen, and nitrogen in Tank 101-SY is the identity of the organic constituents. Ashby et al. (1992) reported the nitrous oxides/hydrogen ratio was in the range 5:1 to 20:1 when HEDTA and EDTA were the principal organic constituents of simulated wastes. Ashby has examined a wide range of model compounds in mechanistic studies of organic degradation reactions, many of which yielded hydrogen as the principal degradation product (Ashby et al. in Schulz and Strachan, 1992). In addition, knowledge of the organic constituents reduced the estimates of the hazards associated with the organic content because the components determined represent a large degradation of the energy associated with the parent organics that were assumed to be present in the waste when the safety analyses were performed. The in-depth analysis of organic species in the tank was necessary for safety and energetics issues that could not be provided by simple TOC analysis alone.

The TOC analysis provides a measure of the fuel content of the waste and can be used as a predictive tool for the amount of heat that could be generated from reactions of the organics with oxidants in the waste such as nitrate and nitrite. The factors that affect the energy released by a chemical reaction between organics and oxidants include the chemical species and chemical mechanism. Currently, acetate is used as the reference organic compound for waste from Tank T-111.

The objective of proposed analyses of waste from Tank T-111 is to determine why portions of waste exhibit unexpectedly high reaction enthalpies, and why the predicted (from tank history) and measured energetics of the waste differ. The strategy proposed to resolve these issues consists of identifying the organic species currently in T-111 that are serving as the fuel. Organic speciation is critical to the evaluation of the potential hazard associated with T-111 waste and determining whether different species other than acetate are present.

In instances where the knowledge of organics is related only to energetics and no problems similar to T-111 are evident, a less specific measure of TOC accountability may be acceptable. In these cases, determination of the functional groups or classes of compounds may be sufficient. Functional group analysis can be performed using techniques that include Raman spectroscopy and Fourier transform infrared spectroscopy. These techniques are in the process of being evaluated for functional group analysis.

Total organic carbon accountability is essential to the safe conduct of waste operations which include interim storage, mitigation, and remediation. Detailed knowledge of relevant physical and chemical properties of organic compounds found to be present in the tanks will provide a scientific basis for classifying and ranking the potential hazards and safety-related concerns for individual tanks with high organic content, and evaluating potential interferences in proposed pretreatment.

Currently, the results of organic analysis and TOC accountability are available from a very limited number of wastes. The level of accountability will be evaluated on an issue by issue basis; different data objectives will require different standards of analysis.

Detailed organic speciation will be required in instances where the data is required to tanks containing a floating organics layer, entrained organic layer nitrite - nitrate organic reactions and flammable gas. The natural objective is to have 100% TOC accountability, but that expectation may be an unrealistic. A more realistic level may be 80-90% TOC accountability. At that point, the cost to account for the rest of the TOC must be weighed with the value of the additional speciation information. That judgment must be made on a case by case basis.

For those cases where the data is strictly used for energetics considerations and calculation of heat release, a 60% TOC accountability may be sufficient. Functional group analysis or compound class identification for the rest of the TOC may also be required.

Efforts during the last several years have concentrated on the development of analytical techniques for the speciation of organics in tank waste and subsequent transfer of technology. This effort has been a costly and time consuming, but extremely beneficial, and should be continued for the next 2-3 years. As the issues pertaining to safety, flammable gas generation, and explosive potential are resolved, the necessity for organic speciation and methods development will diminish. At that point, functional group analysis may become the major thrust of the program. However, if the need arises for speciation, a firm foundation will have been established and little, if any, methods development required.

3.2 Functional Group Analysis

Gas chromatography/mass spectrometry has provided data on the identification of functional groups in tank waste (Campbell et al. 1994). In addition, LC was used to quantitate low molecular weight acids (LMWA) such as oxalic, formic, acetic, and glycolic. Toste et al. (1986) found similar components in Tank 107-AN. Analyses of the organic and aqueous layers from Tank C-103 also indicate the presence of normal paraffin hydrocarbon (NPH), tributyl phosphate (TBP), very small concentrations of alkyl nitriles, and various ketones (Pool et al. 1994). A comprehensive listing of all the chemicals used at the Hanford Site in the period 1944 to 1980 was published by Klem (1990). This list, compiled from historical chemical flowsheets, purchase records, and other chemical records, provided another source for possible functional groups.

The important functional groups that have thus far been identified in tank waste include carboxylates, nitroso, alkanes, phosphates, alcohols, amines, ketones, and nitriles. The order of priority of the functional groups will be dictated by the data objective and will be evaluated on a case-by-case basis. Techniques proposed for functional group analysis will be discussed in the following order: 1) GC/MS, LC, and LC/MS, 2) Raman spectroscopy, 3) Fourier transform infrared spectroscopy (FTIR). The goal is to find a technique that is sensitive enough, quick, and requires minimal sampling handling to identify functional groups in tank waste.

3.2.1 GC/MS, LC, and LC/MS

The techniques of derivatization GC/MS, LC, and LC/MS are used to provide data on the speciation of organic components as well as functional groups.

GC/MS

The chelators and chelator fragments represent a class of compounds whose polarity and nonvolatility precludes direct analysis by GC/MS; therefore, derivatization of the carboxylic acid portion must be performed prior to analysis. Chelators, chelator fragments, and several carboxylic acids have been quantitated in the core segment samples using derivatization GC/MS. The major components detected were ethylenediaminetetraacetic acid (EDTA), nitroso-iminodiacetic acid (NIDA), nitrilotriacetic acid (NTA), citric acid (CA), succinic acid (SA), and ethylenediaminetriacetic acid (ED3A). The chelator of highest concentration was EDTA in all six samples analyzed. The amount of organic carbon accounted for by derivatization GC/MS varied from 20 to 52% of the TOC depending on the sample. Preliminary results indicate the chelators and chelator fragments constitute more of the organic carbon in the convective than the nonconvective layer. High resolution mass spectrometry (HRMS) may also be utilized for functional group analysis. The elemental compositions of 25 components in the derivatization GC/MS total ion chromatogram of tank waste were determined using HRMS. Several nitroso compounds were unambiguously identified; these have been shown to be artifacts. Other functional groups that have been identified in tank waste by GC/MS include alkanes (e.g., normal paraffin hydrocarbon) and phosphates (e.g., tributyl phosphate).

LC

Liquid chromatography has been used to quantitate LMWA (oxalic, formic, glycolic, and acetic acids, which are present in the waste as acid salts). Approximately 23 to 61% of the TOC is accounted for by these acids. Oxalic acid constitutes approximately 40% of the TOC in the nonconvective layer samples. The concentration of oxalate in the nonconvective layer is approximately 3 to 4 times higher than the convective layer. The nonconvective layer sample from the lowest layer has the highest percentage of water-soluble organic carbon as LMWA.

LC/MS

Thermospray LC/MS was used to identify LMWA in actual waste samples. A separation technique was developed using acidic conditions; components identified from the analysis of actual tank waste samples included NIDA, citric, acetic, formic, and glycolic acids. Oxalic acid could not be determined by thermospray LC/MS because the second carboxyl group does not protonate under the separation conditions used, and thus cannot be detected. However, oxalic acid could be detected using plasmaspray (similar to thermospray but with corona discharge for additional ionization) LC/MS. Other LC/MS techniques explored included both plasmaspray and electrospray. Both of these techniques have thus far only been used with standards and have not been used to analyze actual waste samples.

The techniques discussed above are both costly and time-consuming. In addition, extensive sample preparation is usually required. As a result, in those cases where speciation is not required, Raman spectroscopy and infrared spectroscopy are proposed for functional group analysis.

3.2.2 Vibrational Spectroscopy

Raman

Vibrational spectroscopy methods for functional group analysis include infrared (IR) and Raman techniques. These are ideally suited for functional group characterization because of the well-established spectral/structure correlations. Raman and IR have different selection rules, however. Functional groups that typically have weak IR absorbencies give a very strong signal in the Raman spectrum; the opposite is true as well. These strong Raman signals are typically from non-polar functional groups like alkenes. Non-polar functional groups are not affected by hydrogen bonding and other inter- and intra-molecular interactions. As a result, the typical Raman spectrum is composed of bands that are well-defined and insensitive to the chemical environment. This has advantages in certain experiments; for instance, aqueous samples may be characterized without further preparation. Figure 3.1 is an illustration of the Raman spectrometer.

The location of spectral features in the Raman is dependent on the vibrational frequencies of the functional group of the molecule being characterized, and thus the spectral correlations that have been developed for IR can be applied to a Raman spectrum as well. For example, consider the IR and Raman spectra of citric acid shown in Figures 3.2 and 3.3, respectively. The IR spectrum, which was taken from a published source, shows the expected three intense bands in the region between 1690 and 1790 cm^{-1}. In comparison, the Raman spectrum of citric acid also shows a triplet of bands located between 1690 and 1800 cm^{-1}; these may be attributed to the triple carboxyls as well. The resolution of these bands in the Raman spectrum is significantly better than the IR spectrum, partly due to the instrument resolution.

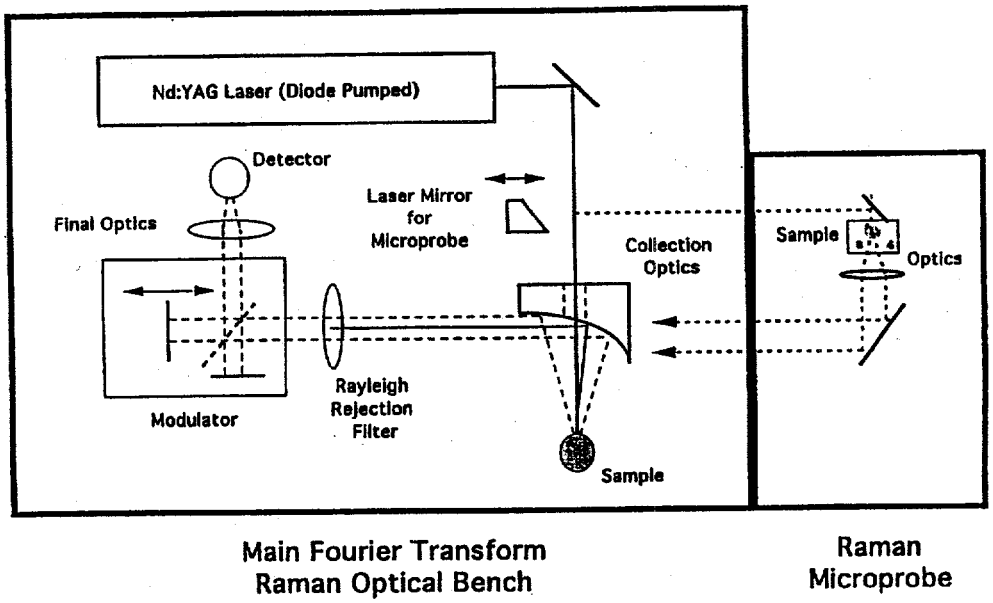


Figure 3.1. Schematic of Raman Spectrometer

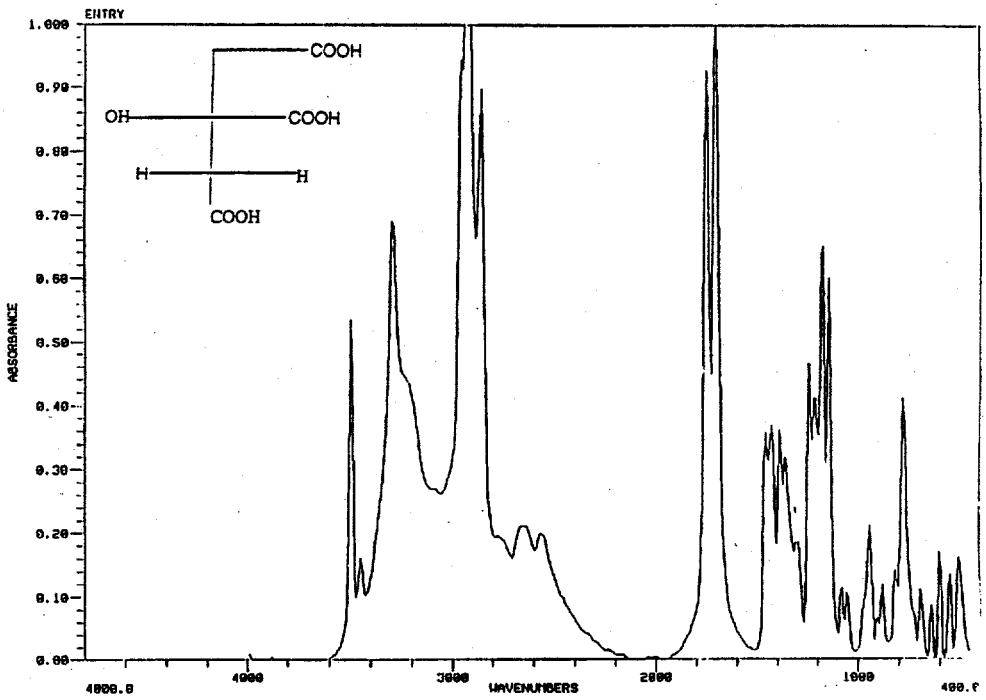


Figure 3.2. IR Spectrum of Citric Acid

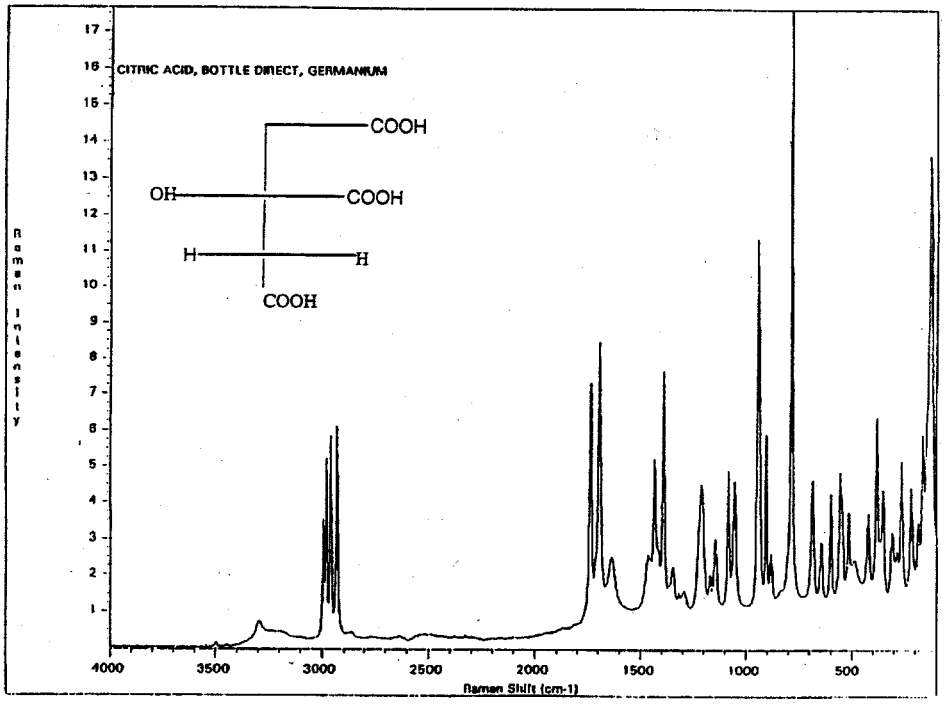


Figure 3.3. Raman Spectrum of Citric Acid

Thus, it is expected that several functional groups that are of interest in tank waste may be characterized without speciation using Raman spectroscopy requiring much less time and sample handling than currently utilized GC/MS, LC, and LC/MS techniques. Such groups include:

- Carbonyls: This group includes carboxylic acids, anhydrides, aldehydes, ketones, amides, and esters. In general, these groups have strong bands in the Raman and, in particular, the IR. The carbon-oxygen double bond is readily apparent in the range between 2000 and 1650 cm^{-1}. This region is generally clear of other functional groups, and thus a band in this region is highly diagnostic. Characterizing the functional group more fully depends on the presence (or lack) of other bands.

  - Carboxylic acids: Typically, the carbonyl appears in the spectrum between 1750 and 1690 cm^{-1}, with the C-O bond appearing between 1310 and 1200 cm^{-1}. If the carboxylic acid is ionized (which will occur if the tank waste is highly basic) the bands are shifted to between 1650 and 1550 cm^{-1} for the first band and between 1450 and 1400 cm^{-1} for the second band.

  - Anhydrides: These typically are present between 1850 and 1700 cm^{-1}. The second band is located in the same 1310 to 1200 cm^{-1} region as the carboxylic acids.

  - Aldehydes and ketones: The carbonyl band from these groups appears in the spectrum between 1720 and 1650 cm^{-1}. More diagnostic is the lack of a major band in the 1300 cm^{-1} region, which distinguishes aldehydes and ketones from a carboxylic acid type moiety (ie., anhydrides, esters, etc.).

  - Amides: The carbonyl diagnostic band of an amide is usually found between 1750 and 1800 cm^{-1}, unlike the other carbonyl functional groups except for anhydrides. It should be noted, however, that there will be no carbon-oxygen single-bond band, and there will be a band located in the region 3500 to 3100 cm^{-1} from the nitrogen-hydrogen stretch.

  - Esters: These have spectral features that are essentially identical to the carboxylic acids, and, as such, will be difficult to distinguish. A possible solution will be to change the pH of the waste and determine if any peaks shift. An example of an ester, methyl ester of IDA, is shown in Figures 3.4 and 3.5.

  - Nitroso groups: By correlation with the IR spectrum, it is expected that the Raman spectrum will have a band at approximately 1450 cm^{-1}. A comparison of the spectrum of IDA and its N-nitroso analog, NIDA, shows a large band at 1490 cm^{-1} in Figure 3.6. There is a second intense band in the NIDA spectrum at 1150 cm^{-1} that is not expected in the IR; this band may be attributed to one forbidden in the IR.

  - Alkenes and alkynes: The alkenes are expected to have an intense Raman band at approximately 1650 cm^{-1}. Alkynes have intense Raman bands at approximately 2250 cm^{-1}. In both cases the bands may be shifted toward the far-IR by conjugation or the presence of other functional groups.

  - Peroxides. Peroxides have spectral bands in the 1000-cm^{-1} to 900-cm^{-1} region of the spectrum depending on the substituents.

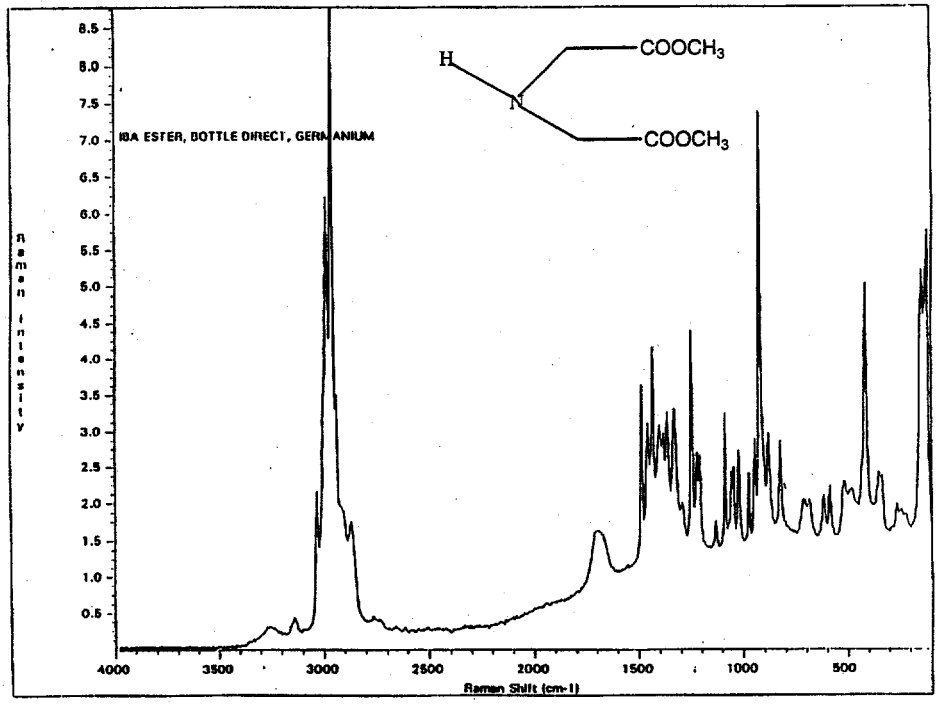


Figure 3.4. Raman Spectrum of Methyl Ester of IDA

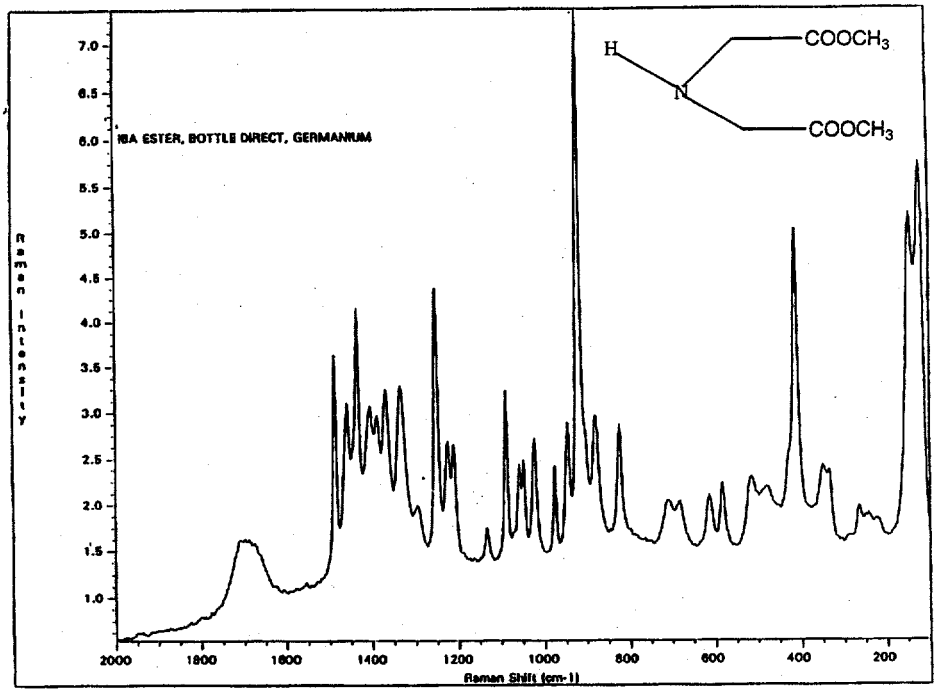


Figure 3.5. Raman Spectrum of Methyl Ester of IDA

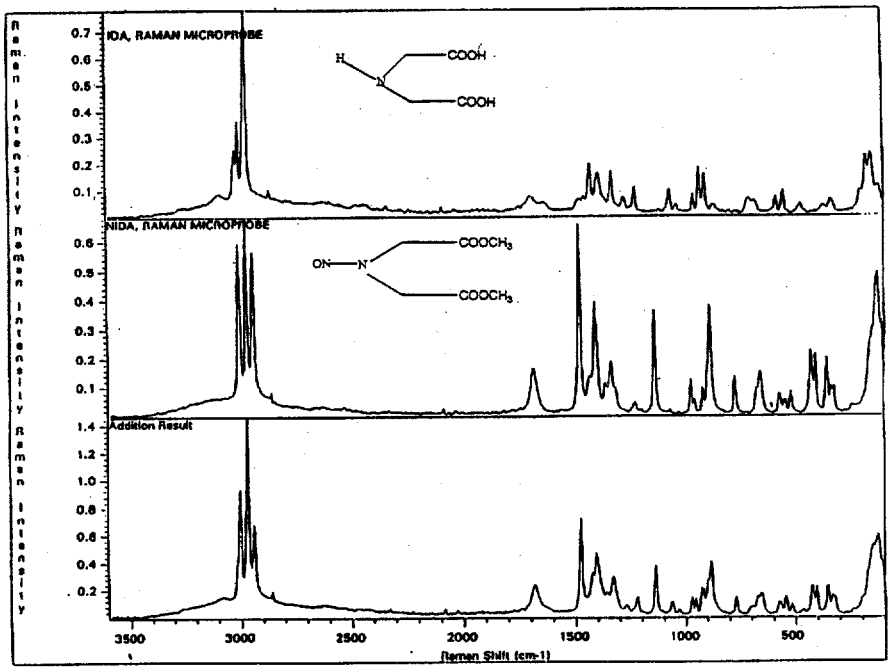


Figure 3.6. Spectrum of (a) IDA, (b) NIDA

- Nitro groups. These give very strong Raman bands in the range of 1390 to 1330 cm^{-1}, with a dependency on the whether the nitro group is attached to an aliphatic or aromatic functionality.

- Nitrile groups: These give intense bands in the region of 2300 cm^{-1}.

It should be noted that detecting the presence of a functional group in a sample is dependent on several factors that include the kinds of chemicals that are present, their relative concentrations, and the complexity of the spectrum from each individual component. For example, the spectra of sodium nitrite and EDTA are attached shown in Figures 3.7. and 3.8, respectively. As can be seen, the nitrite spectrum is very simple, with only two very sharp peaks, while the spectrum of EDTA is very complex. The spectrum of a complex mixture may be simplified by using suitable data-processing techniques. For instance, it is very possible to strip the spectrum of a major component by spectral subtraction; alternatively, applying a multi-variate technique like Principal Components Analysis (PCA) can also yield valuable insights into the components of a mixture.

Another factor to consider is sensitivity. Conventional Raman is not as sensitive as other techniques. However, in cases in which the data is used for energetics or calculation of heat release, the technique may be sensitive enough to determine functional groups. Recent work has increased the sensitivity of Raman to the nanogram range. This technique is referred to as surface enhanced Raman spectroscopy (SERS), a comparatively simple technique that places the sample on a roughened metal surface. The interaction between the metal atoms and the molecular bonds greatly strengthens the Raman signal.

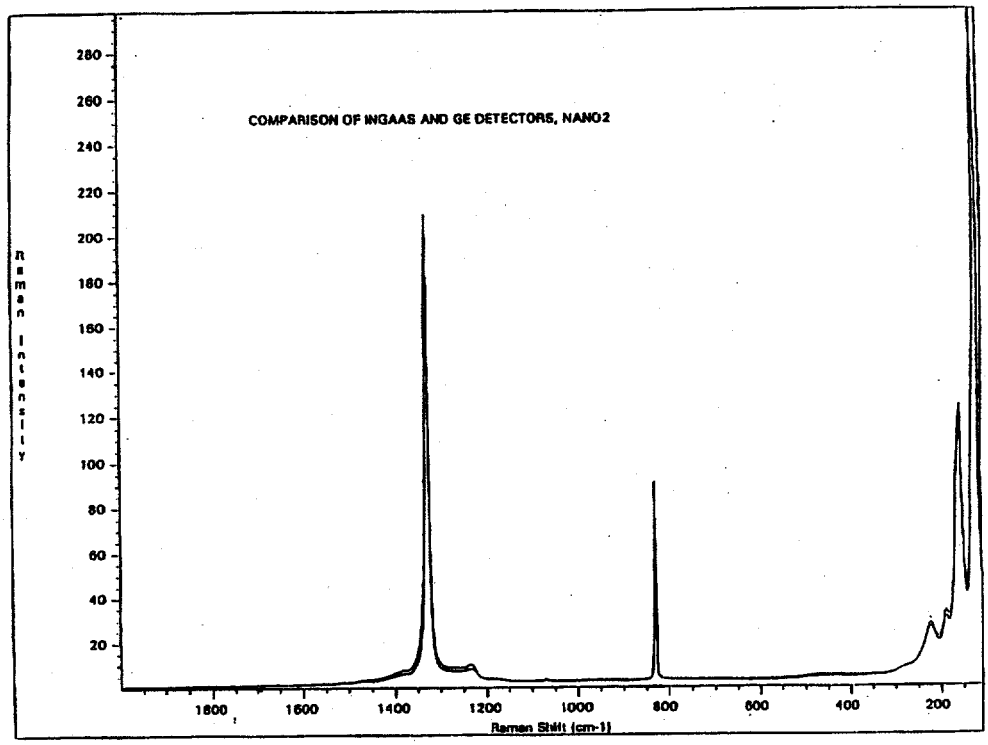


Figure 3.7. Spectrum of $NaNo_2$

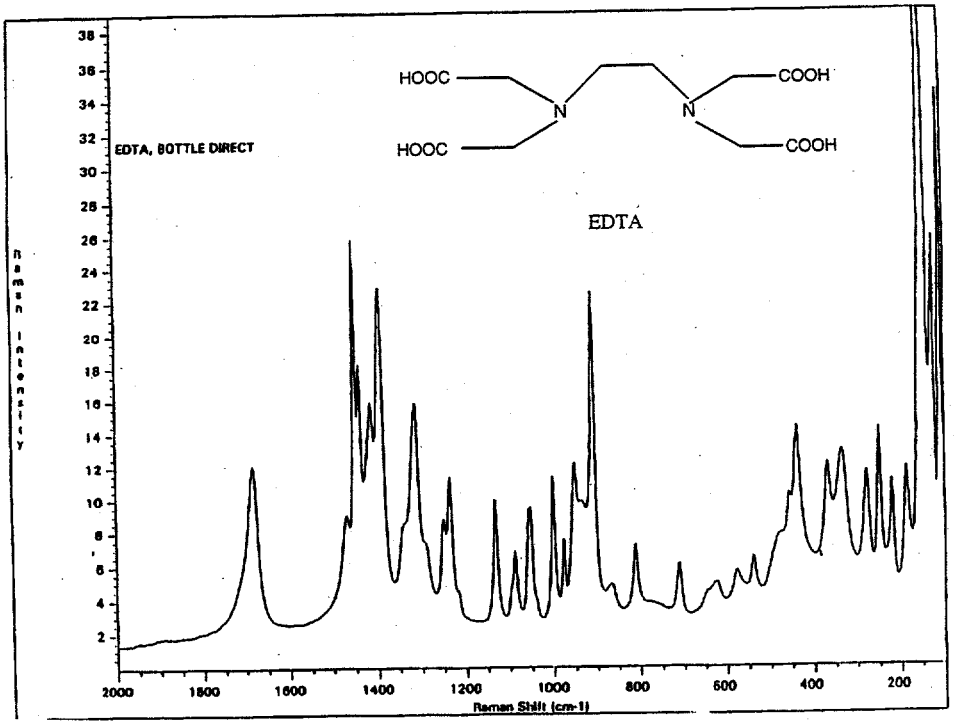


Figure 3.8. Raman Spectrum of EDTA

Overall, it is expected that Raman will greatly complement the other techniques currently used to characterize waste samples such as derivatization GC/MS and LC. Raman uses well-defined structure-spectrum correlations and has added advantages in that samples may be characterized with minimal sample preparation. To analyze radioactive samples, a fiber optic coupled sample compartment will be utilized. This will permit the sample to be analyzed using standard radiological procedures.

IR

The strongest IR absorptions are due to functional groups that have a relatively large dipole. Thus, it is expected that IR will have the most sensitivity to the following functional groups:

- Carbonyls (1800 to 1690 cm^{-1}): The exact location of the carbonyl peak can be used to identify whether or not the group is from an organic acid, ketone, aldehyde, lactone, amide or other such functionality.

- C-O bond (1200 to 1000 cm^{-1}): Depending on the exact location of this peak, it is suggestive of an organic acid, esters and ethers.

- Halogens (850 to 600 cm^{-1}).

Other groups that are amenable to analysis by IR are nitro and nitrate groups and amines.

When it is necessary to characterize a mixture, the vibrational methods have the same difficulties as methods like mass spectrometry because the information yielded will be an aggregate of all the components that are present. Deciphering a spectrum of a mixture is complicated by the fact that the spectral response is generally correlated to the concentration of the material present, and thus minor components may not be detected. This may not be critical if the data is used to determine thermal content of waste. The location of the absorption of a particular functional group in the spectrum will be approximately the same for all molecules, and thus it is nearly impossible to get information about a specific molecule. In addition, the responses of the various functional groups differ. A carbonyl group will, for instance, be strongly absorbing in the IR while a carbon-carbon double bond will be extremely weak. A weakly-absorbing functional group in a low-concentration component may not be detectable.

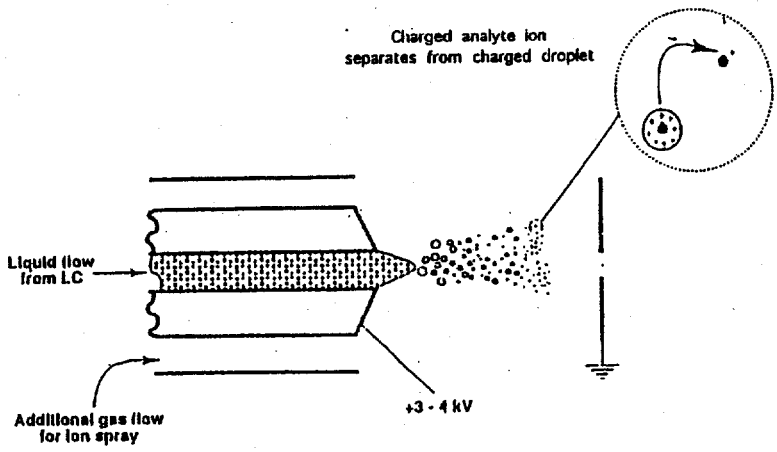
One solution to this problem is to use spectral data manipulations to remove or make more apparent the individual components of a mixture. A more direct solution to this problem is to use a separation technique like gas chromatography in series with the vibrational method. As a class, these combined methods are referred to as hyphenated techniques. Several of the vibrational hyphenated techniques are very mature and thus are well-characterized and easy to apply. Fourier transform infrared (FTIR) spectroscopy has proven to be more amenable to being mated to a chromatographic technique because of its greater sensitivity.

For those cases where the data is strictly used for energetics considerations and calculation of heat release, a 60% TOC accountability may be sufficient. Functional group analysis or compound class identification for the rest of the TOC may also be required. Situations may also arise where only functional group analysis may be required to address the particular concern or data objective. In those instances, functional group analysis will be performed using Raman spectroscopy and Fourier transform infrared spectroscopy. These techniques will provide the most efficient analysis scheme for functional group analysis.

For the past several years, efforts have concentrated on the development of analytical techniques for the speciation of organics in tank waste and subsequent transfer of technology. Although the efforts have been costly and time consuming, they have been extremely beneficial and should be continued for the next 2-3 years. As the issues pertaining to safety, flammable gas generation, and explosive potential are resolved, the necessity for organic speciation and methods development will diminish. At that point, functional group analysis may become the major thrust of the program. However, if the need arises for speciation, a firm foundation will have been established and little, if any, methods development will be required.

3.3 Electrospray MS

As previously stated, derivatization GC/MS for the analysis for the analysis of chelators and chelators fragments, although very successful, is both time-consuming and labor-intensive. A new ionization method recently acquired on the JEOL SX102/SX102 mass spectrometer is electrospray ionization (ESI), an effective method of analyzing nonvolatile analytes in solution by mass spectrometry without prior derivatization (Smith et al. 1991). This technique has been widely utilized in the biochemical community for the analysis of intact peptides, proteins, glycoproteins, and oligonucleotides, which were previously beyond the capabilities of mass spectrometric ionization techniques due to their thermal lability and nonvolatility (Edmonds and Smith 1990, Kebarle and Tang 1993). The electrospray process involves applying a high voltage (3-5 kV) to a metal capillary through which analytical solution is delivered (μL/min). The electric field gradient between the metal capillary and the inlet to the mass spectrometer produces a spray of charged droplets. These droplets contain charged analyte ions that undergo desolvation resulting in gas-phase analyte ions representative of the ions in solution. A schematic representation of this ionization technique is shown in Figure 3.9. Figures 3.10 and 3.11. illustrate the JEOL ESI source.



Adapted from: Practical Organic Mass Spectrometry - A Guide for Chemical and Biochemical Analysis, 2nd Ed., J.R. Chapman

Figure 3.9. Representation of Electrospray Ionization

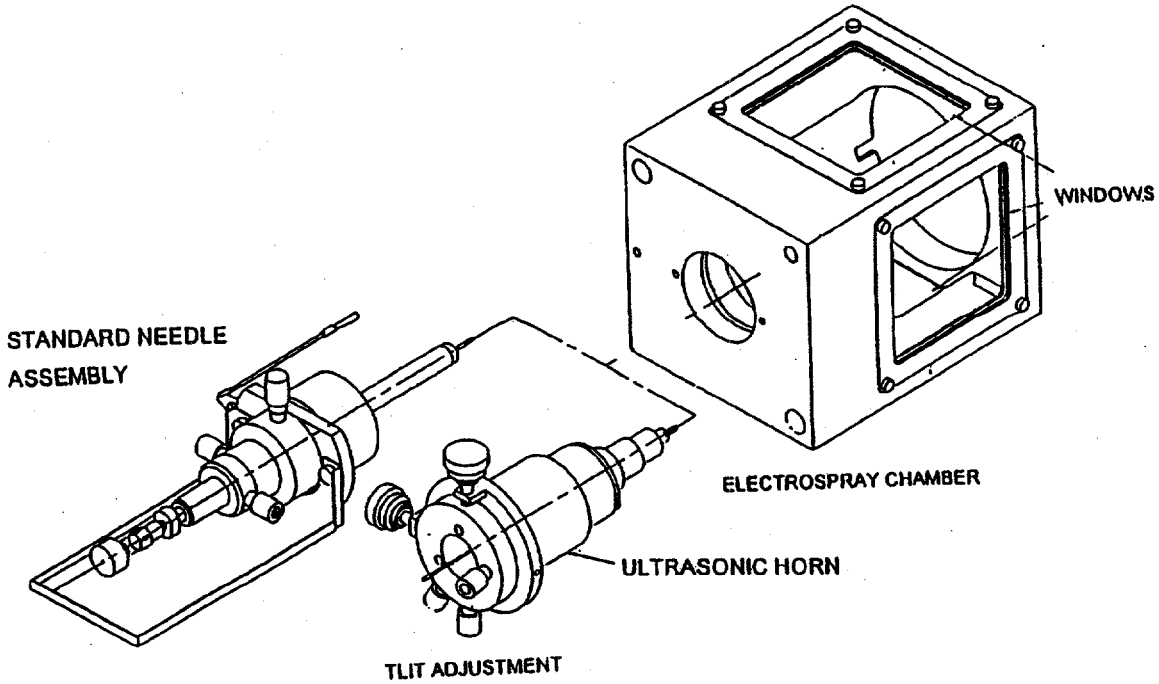


Figure 3.10. JEOL ESI Source (Outer)

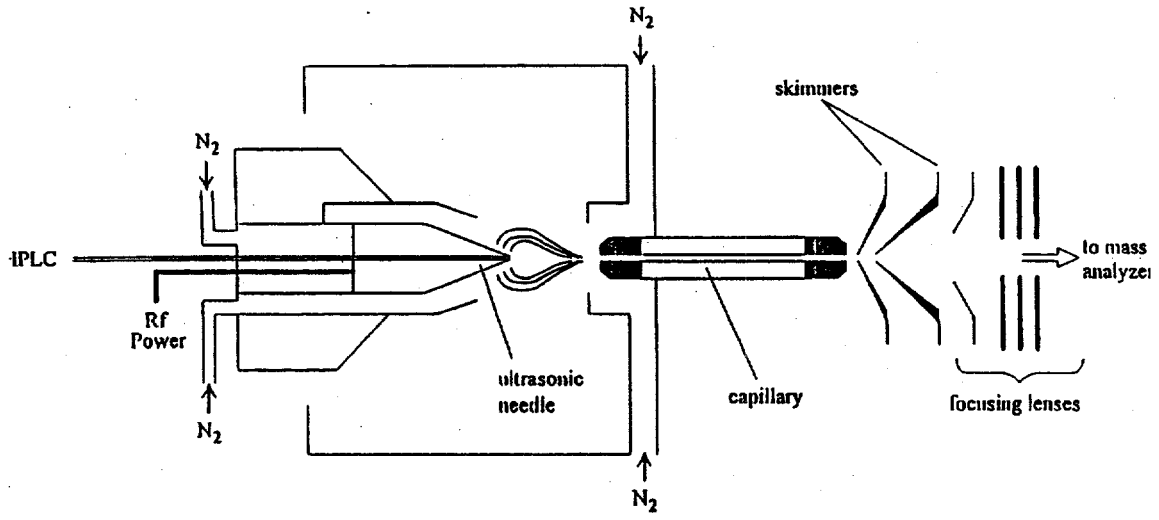


Figure 3.11. JEOL ESI Source (Inner)

A characteristic of this ionization process is the production of multiply protonated ions, often resulting in a charge state distribution for each analyte species. The production of gas phase ions are indicative of species present in solution, and the observation of sodium or potassium adducted analyte species when these salts are present in solution. Electrospray ionization is a sufficiently gentle ionization technique to transfer noncovalent, weak associations present in solution into the gas phase (Smith and Wahl 1993, Light-Wahl et al. 1994). Therefore, ESI-MS can be utilized for studying solution associations and characteristics.

The continuous solution flow required for this ionization technique makes ESI amenable to interfacing with separation techniques such as LC and CE. One potential difficulty in applying ESI-MS to the analysis of complex high-salt solutions is the competition that may occur between analyte species and buffer components for ionization efficiency. However, the combination of ESI with on-line separation techniques may serve to minimize these difficulties. Preliminary results of applying ESI-MS to the analysis of specific nonvolatile analytes of interest, such as ethylenediamine tetraacetic acid (EDTA) show promise for this analysis technique. In addition, the gentleness of the ESI process allows for the preservation of solution associations such as metal-chelator complexes and weak noncovalent associations during the ionization process and transfer into the gas phase. Therefore, ESI-MS is very useful for probing the occurrence and identity of solution associations difficult to probe by other mass spectrometric techniques.

3.3.1 Electrospray Ionization Mass Spectrometric Detection of Chelator Species

Electrospray ionization MS data of the chelators was obtained on the JEOL SX102/SX102 mass spectrometer fitted with an ESI source. This technique is being applied to the analysis of chelators as shown in Figures 3.12 to 3.18. The instrumental conditions were as follows: magnetic field scanned from 0-2000 Daltons, 30 ms cycle time, data accumulated for approximately three minutes, negative ion mode detection. The sample solutions were made by dissolving stock chelators in 25%/75% isopropanol/water with a final chelator concentration of 1mM, unless otherwise noted. The solutions were continuously infused to the ESIsource at 1-2 μL/min. A counterflow of heated N_2 was used to aid in desolvation.

The negative ion ESI-MS spectrum of 1mM EDTA in 25%/75% isopropanol/water is shown in Figure 3.12. The singly and doubly charged ions of EDTA are the predominant ions observed. The negative ion ESI-MS spectrum of HEDTA is shown in Figure 3.13. with the singly charged HEDTA ion as the predominant species. The ESI-MS of the ethylenediaminediacetic acid (EDDA) solution (Figure 3.14) shows both the EDDA and ED3A ions. The ED3A species is most likely present in solution as an impurity. The clusters of EDDA (labeled as dimer, trimer and tetramer of EDDA) could be the result of mild interface conditions in the ESI process. Nitrilotriacetic acid (NTA) gives a singly charged parent ion by ESI-MS as shown in Figure 3.15. In addition a solvent ion of isopropanol (deprotonated) is observed. The disodium and tetrasodium EDTA solutions are also amenable to direct analysis by ESI-MS, as evidenced by the spectra in Figures 3.16. and 3.17., respectively. Addition of $Fe(NO_3)_3$ to the tetrasodium EDTA solution results in the complexation of EDTA with Fe. This Fe-EDTA complex is observed by ESI-MS, as shown in Figure 3.18. The NO_3^- counter ion is now the base ion in this solution, but the ions of interest are still observed at higher *m/z*.

The preliminary results from ESI-MS indicate it may be very useful for the direct analysis of chelators and chelator fragments. Further work to develop separation techniques is underway.

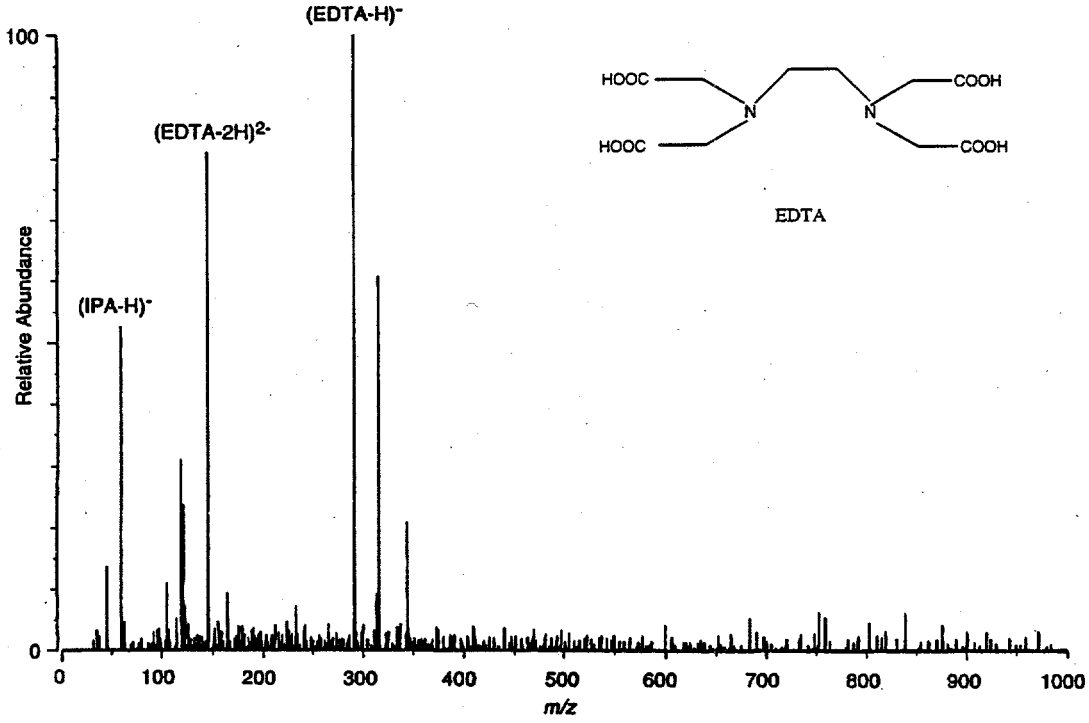


Figure 3.12. ESI-MS Spectrum of EDTA

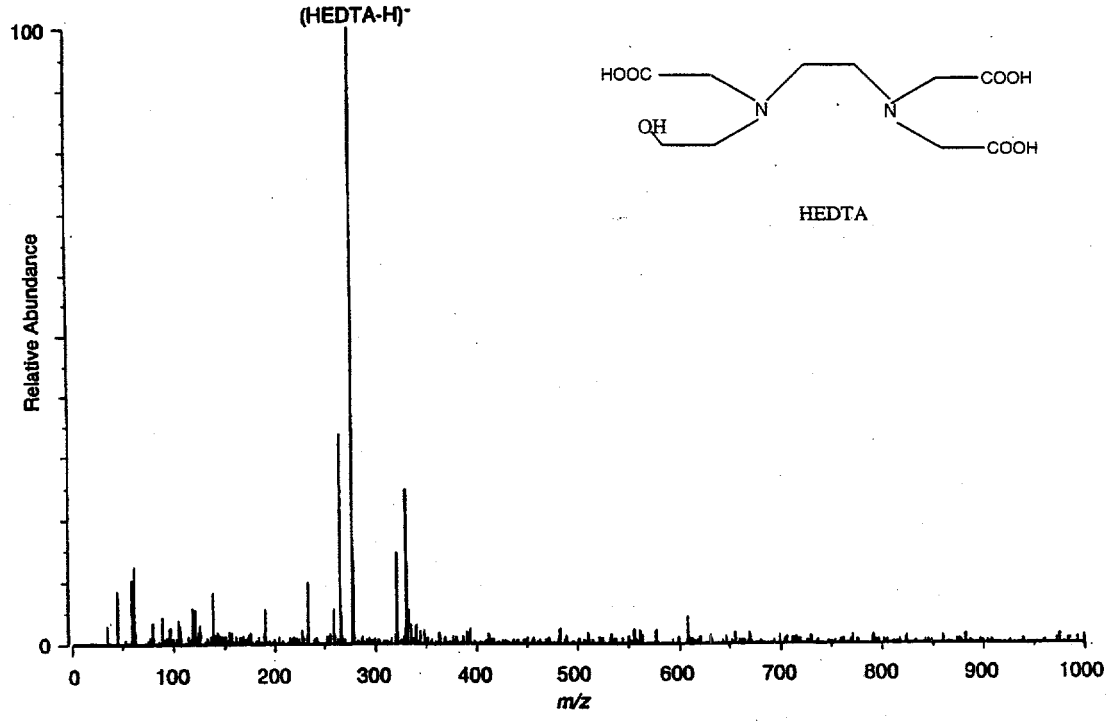


Figure 3.13. ESI-MS Spectrum of HEDTA

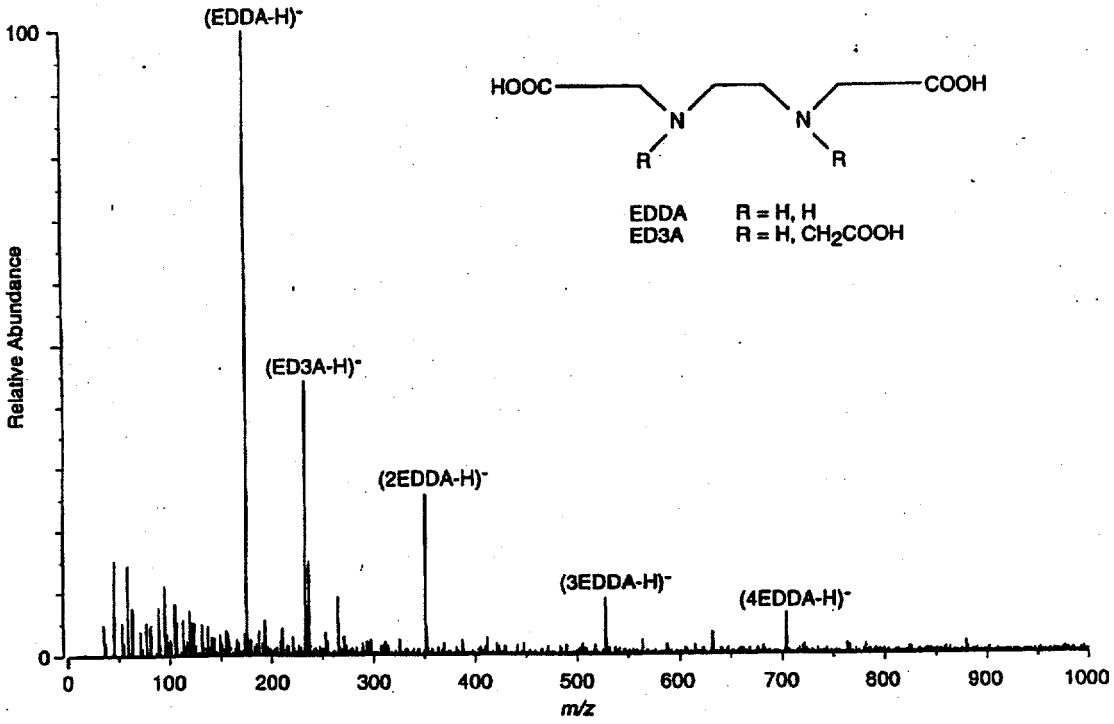


Figure 3.14. ESI-ME Spectrum of EDDA and ED3A

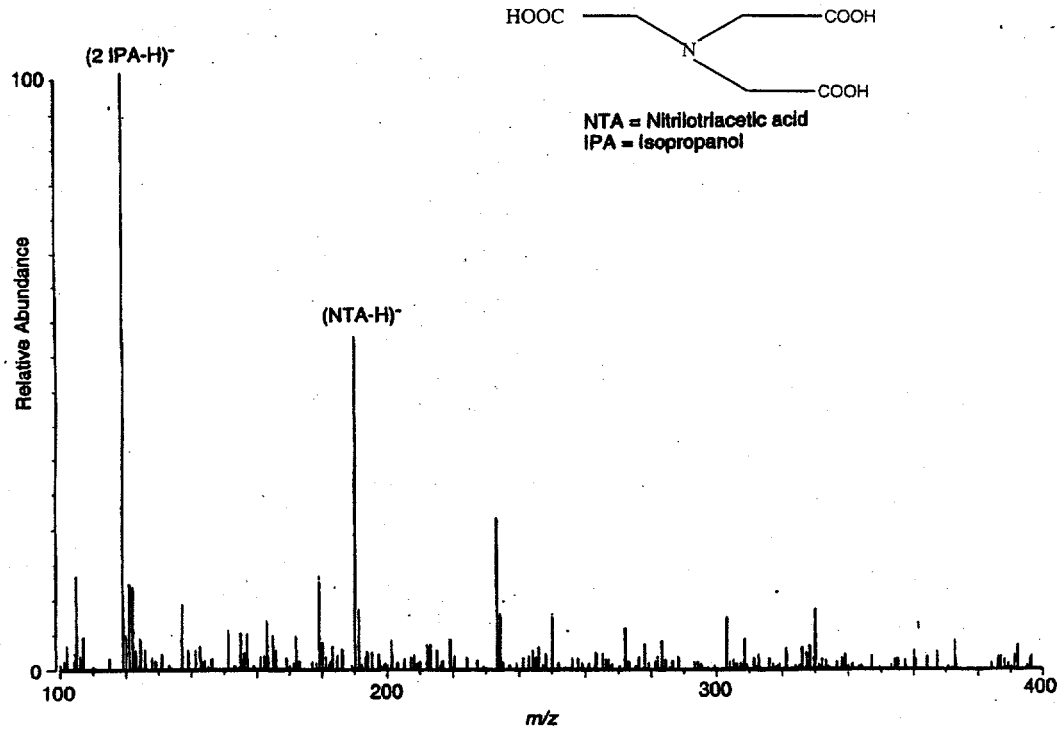


Figure 3.15. ESI-MS Spectrum of NTA

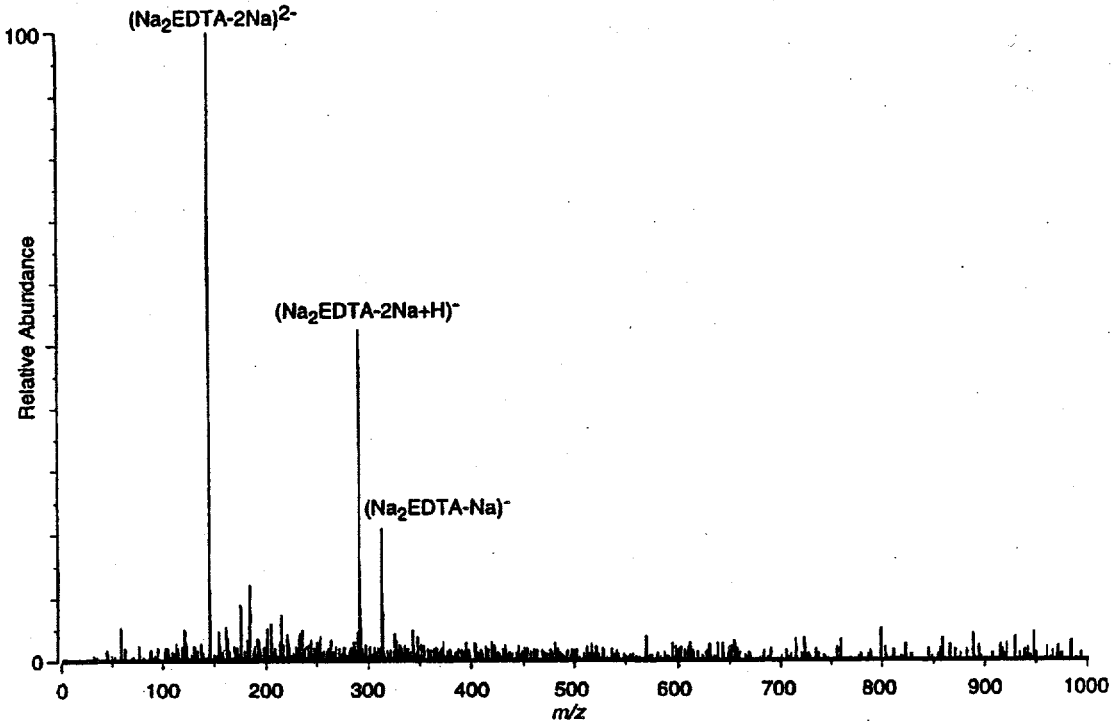


Figure 3.16. ESI-MS Spectrum of Disodium EDTA

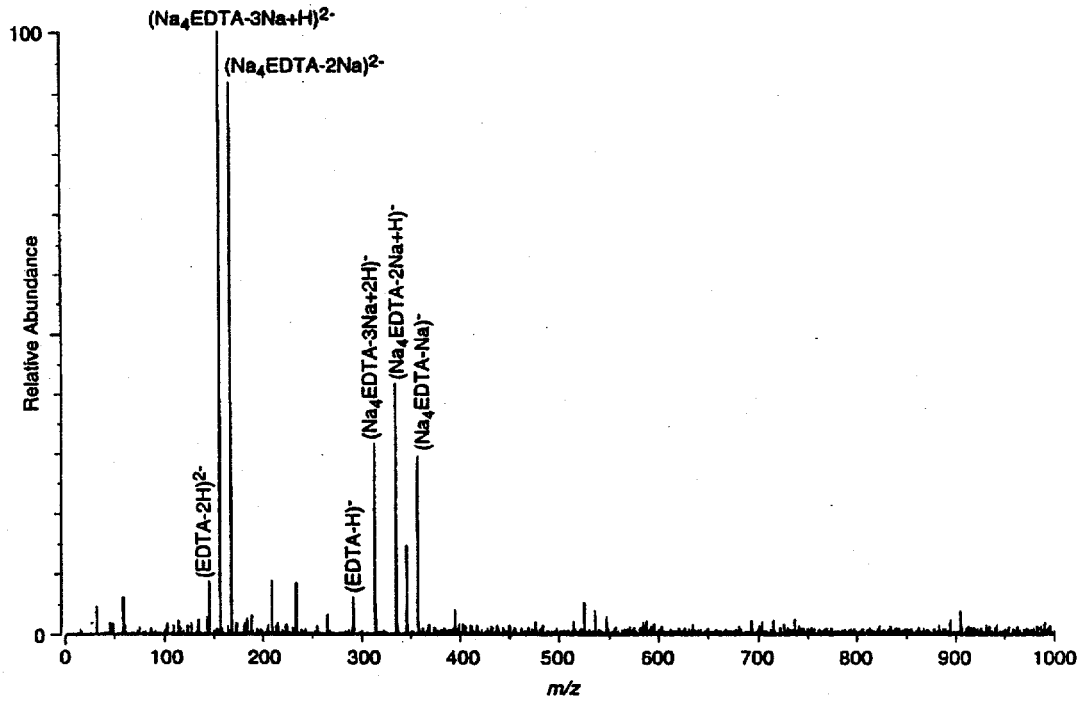


Figure 3.17. ESI-MS Spectrum of Tetasodium EDTA

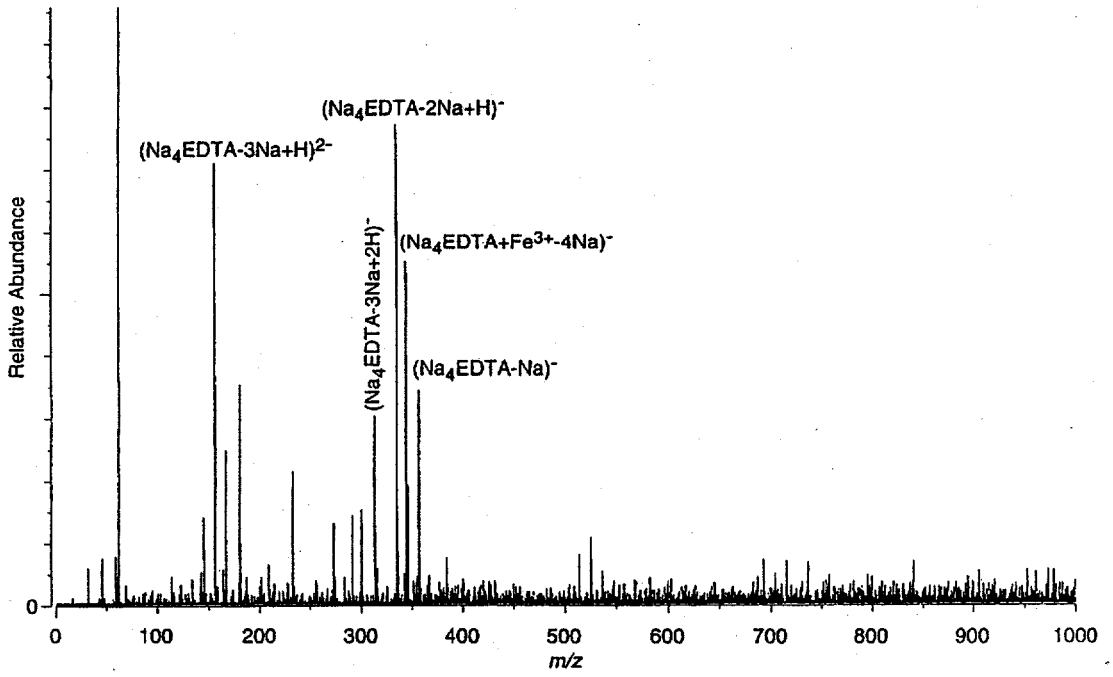


Figure 3.18. ESI-MS Spectrum of Fe-EDTA

3.4 Supercritcal Fluid Extraction

The procedure for the analysis of chelators and chelator fragments using derivatization GC/MS produces large amounts of waste, and the derivatives have a limited lifetime. Derivatization, followed by supercritical fluid extraction, offers advantages to limit waste production and disposal, increase the lifetime of derivatives, and separating the radioactive components.

Supercritical fluid extraction uses highly pressurized carbon dioxide (CO_2), or other fluids, to extract organics from a variety of matrices. As part of the extraction process the supercritical fluid is allowed to vaporize; therefore there is little or no solvent waste to be disposed of at the conclusion of the extraction. This feature is particularly attractive in light of the efforts to reduce chemical waste.

Carbon dioxide SFE has been used successfully for several years to extract nonpolar and semi-polar materials from complex matrices. Supercritical CO_2 is not as effective in removing highly polar materials like small organic acids. This limitation, however, can be circumvented by chemically modifying these difficult species to a less polar form before SFE is performed. This chemical modification can be performed using a supercritical fluid on the target species while they are still contained in the sample matrix. This technique, which is referred to as in-situ derivatization SFE, has been used successfully by other investigators on small organic acids like oxalic acid. Preliminary work in our laboratory has demonstrated that in situ derivatization SFE is capable of derivatizing species like EDTA, which can then be removed from the sample matrix. The full development of this procedure will allow SFE, with its low waste generation, to be applied to characterizing tank waste and other mixed wastes. A more detailed discussion is included of the theory and practice of SFE, the status of

the use of the in situ derivatization technique in our laboratory and what the likely impact of the full development of the technique will be on waste characterization efforts.

Supercritical fluids may be defined as gases that are near their critical temperature and are compressed to pressures (or densities) at which liquid-like interactions become significant. The combination of physical properties (viscosity and diffusion rates) with variable solvent properties provides the basis for the advantages of SFE. By control of pressure and temperature, the physical properties of a supercritical fluid are variable between the limits of a normal gas and those of a liquid. Different solvent characteristics may be displayed at each density. Typically, supercritical fluids are used at densities ranging from 0.1 to 0.8 of their liquid density. Practical pressures for applications range from less than 50 bar to more than 500 bar. Under these conditions the diffusion coefficients (diffusivity) of supercritical fluids are substantially greater than liquids. For example, the diffusivity of supercritical CO_2 varies between 10^{-4} and 10^{-3} cm^2/s over the range of conditions usually utilized. Liquids typically have diffusivities of less than 10^{-5} cm^2/s. Similarly, the viscosity of supercritical fluids mirrors the diffusivity and is typically 10-100 times less than liquids (McHugh and Krukonis 1986). These more favorable physical properties provide the basis for extraction and fractionation.

The pressure-density relationship for CO_2 in terms of reduced parameters (e.g., pressure, temperature, or density divided by the appropriate critical parameter) is shown in Figure 3.19. (HP SFE Manual 1990). This relationship is generally valid for most single-component systems. The isotherms at various reduced temperatures show the variations in density that can be expected with changes in pressure. The density of a supercritical fluid will be typically 10^2-10^3 times greater than that of the gas at ambient temperatures. As a result, molecular interactions increase because of shorter intermolecular distances. The liquid-like density of a supercritical fluid results in enhanced solvating capabilities. The variable solvent properties as a function of density have been demonstrated for a

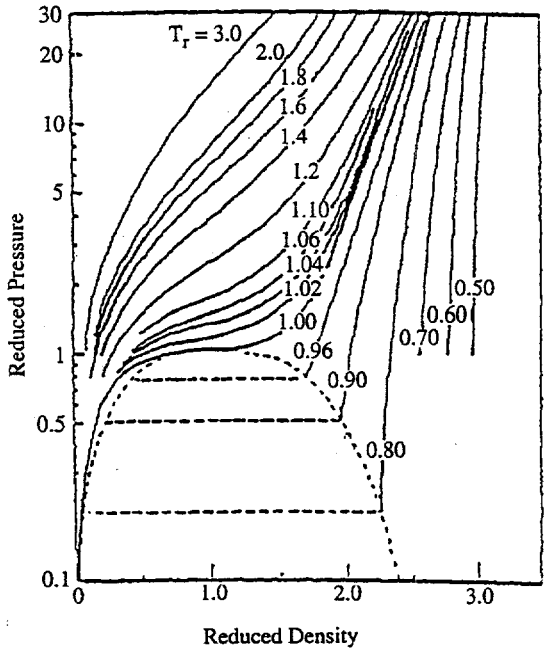


Figure 3.19. Pressure-density Relationship of Carbon Dioxide Expressed in Terms of Reduced Parameters

number of fluids using the solvatochromic method (Yonker et al. 1986). The relationships between pressure, temperature, and density can be estimated with reasonable accuracy from equations of state for a pure supercritical fluid, as well as for infinitely dilute supercritical fluid solutions relevant to chromatographic separations and extractions.

The range of solvating power of supercritical fluids is of primary importance and essentially defines the limit of application. The use of a supercritical fluid composed of only CO_2 is highly selective for nonpolar molecules. To extend the solvating power of SFE,it is often advantageous to use a binary fluid mixture. The effect of introducing a second component in the CO_2 supercritical fluid is increasing the range of molecular species that are soluble in a single supercritical fluid or altering the critical temperature of the mobile phase. This, in turn, alters the density of the supercritical fluid at that temperature. The phase behavior of binary systems is highly varied and much more complex than single-component systems. Five basic types of phase behavior have been identified, with the simplest type characterized by a continuous mixture curve for pressure and temperature conditions over the composition range of the two components. An example of a supercritical binary mixture is CO_2 with either isopropanol or methanol. The phase behavior of CO_2-methanol is shown in Figure 3.20., which gives the pressure-composition vapor-liquid envelopes for three temperatures. The single-phase supercritical regions are above the envelopes, and the regions within the envelopes correspond to two-phase subcritical mixtures at the respective temperatures. It is essential that the fluid mixtures used for mobile phases be selected so they can be mixed and pumped as a single phase, preferably at ambient temperatures to exploit the advantages of supercritical fluids. Proper operating conditions must also be chosen that will give a single-phase supercritical fluid; care must be taken when operating over a range of pressures to avoid entering a two-phase region (Brunner 1985; Seckner 1987).

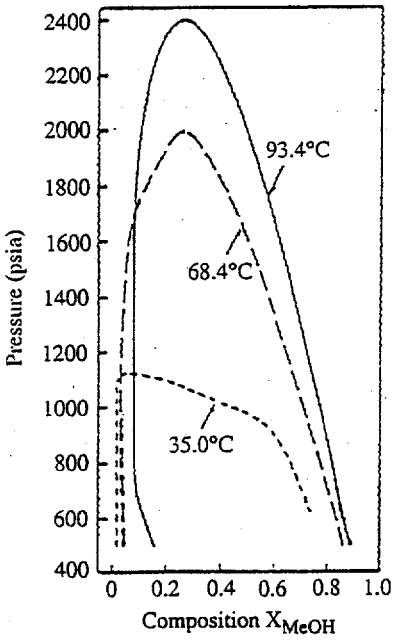


Figure 3.20. Pressure Composition Diagram for Carbon Dioxide-Methanol Fluid Mixtures at three Temperatures

In addition to controlling the supercritical fluid composition, increasing the supercritical fluid density increases analyte solubility. A maximum rate of increase in solubility with pressure is observed near the critical pressure, where the rate of increase of density with pressure is greatest (Gitterman and Procaccia 1983). There is often a linear relationship between the log [solubility] and fluid density for dilute solutions of nonvolatile compounds. Where volatility is extremely low, and at densities less than or near the critical density, increasing temperature will typically decrease solubility (Smith and Udseth 1983). However, solubility may increase at sufficiently high temperatures, where the solute vapor pressure also becomes significant. Solubility generally increases with temperature under conditions of constant density. The highest supercritical fluid densities at a constant temperature are obtained near the critical temperature; the greatest solubilities will often be obtained at somewhat lower densities but higher temperatures. Similar to liquids, more polar solutes are most soluble in polar supercritical fluids, although nominally nonpolar fluids can be remarkably good solvents for moderately polar compounds (McHugh and Krukonis 1986). Carbon dioxide, for example, at higher pressures can exhibit solvating properties intermediate between liquid pentane and methylene chloride. This suggests that some polar solvents may make good supercritical fluids. However, many polar solvents that would be attractive fluids have critical temperatures that are excessively high to allow practical application. Thus, CO_2 remains the best choice for a supercritical fluid, although additional components may be introduced to modify the properties of the fluid.

It is useful to review the current techniques used for chelator analysis to more fully appreciate the potential benefits of a SFE based approach. As part of the Flammable Gas Safety Program, the chelators (e.g., EDTA) and chelator fragments (oxalic acid for instance) in radioactive waste have been characterized using derivatization GC/MS. Chelators are highly polar species; therefore, they do not chromatograph very well. The samples have to be alkylated prior to analysis. Because these samples are part of a mixed hazardous waste, a hot cell extraction/Radiochemical hood derivatization of chelators and chelator fragments (Campbell et al. 1994) procedure was developed. In this procedure, approximately 5 g of waste is stirred with 10 mL of doubly-distilled water overnight. The aqueous phase is filtered and then passed through a cation ion exchange column containing 10 gr of resin. The column is then rinsed with an additional 10 mL of water to bring the total volume to 20 mL. This is then split into 2-mL aliquots which are then evaporated to dryness using dry nitrogen and heat; the drying process can require up to one week to complete. The samples are then derivatized by adding 2 mL of BF_3/methanol and heating for one hour at 100°C. At the end of this time, 2 mL of 0.1 M KH_2PO_4 solution is added. This solution is then extracted using 1 mL of chloroform. Thus, from this process, approximately 10 mL of radioactive liquid waste and at least 10 grams of radioactive solid waste are generated. Ideally, a replacement method that minimizes the amount of labor and waste must be found.

Because SFE could reduce the amount of labor required to perform a chelator analysis, the use of this method was explored. It was found, however, that the commonly found chelators (EDTA, oxalic acid, etc.) were not amenable to extraction by SFE due to their polarity. Preliminary work in our laboratory has identified a possible method that will allow the full benefits of SFE to be applied to the extraction of organic acids from mixed wastes as a prelude to characterization. Several authors have demonstrated the use of in situ SFE derivatization to make highly polar compounds more amenable to SFE extraction (Rochette et al. 1993; Field et al. 1992; David et al. 1992; Lee et al. 1992; Hawthorne et al. 1992; Hills et al. 1991). In in-situ derivatization SFE, the target analyte is derivatized prior to extraction while the analyte is still in the sample matrix. The reagents used for the in situ derivatization are the reagents commonly used for alkylation including BF_3/MeOH. The authors indicated that there was an excellent chance that the in-situ derivatization/SFE technique might work on tank wastes.

In particular, Hill showed that oxalic acid and 2-hexenedioic acid could be derivatized and removed from coffee beans, which is a complex sample matrix. To examine this possibility, a simple model system consisting of EDTA and lauric acid in sand was extracted. These compounds were derivatized using BF_3/MeOH and extracted under SFE conditions. It was found that EDTA and lauric acid were successfully derivatized and subsequently extracted from the sand, a test matrix, is shown in Figure 3.21. The mass spectra obtained for the methyl esters of EDTA and lauric acid are shown in Figures 3.22. and 3.23., respectively. Although a rigorous recovery study was not made, it was estimated that the recovery of the EDTA was approximately 100%. It is also expected that any radioactive isotopes would remain in the matrix being extracted; that is, the extracted organic acids would have been free of radiological activity.

The successful development of in situ SFE for the analysis of chelators would have two immediate benefits; namely, a reduction in time and labor required to do the analysis, and a reduction in the amount of chemical waste that would have to be disposed. As a first step, it will be necessary to optimize the derivatization conditions using BF_3/methanol and the optimal conditions for the subsequent removal of the alkylated species by SFE. Another possible additional benefit of this work will be the development of selective extraction conditions for the various chelators. Alternatively, it may be possible to develop conditions that will allow for the selective removal of other organic species separate from the chelators. The development of such a method will allow for a more accurate accounting of the organic carbon in the molecule. In addition to the work with BF_3/MeOH, the use of other alkylation reagents should be explored as well. The use of ion pairing reagents should be evaluated. These ion pairing materials form the basis of a HPLC method for chelator analysis. It is therefore reasonable

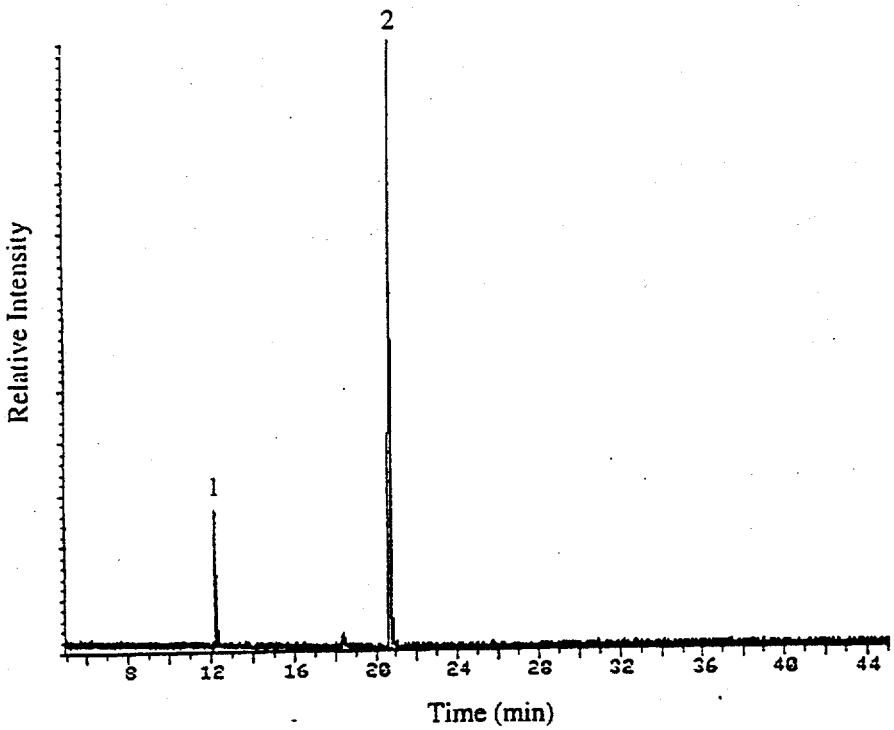


Figure 3.21. Total Ion Chromatogram of Derivatized (1) Lauric Acid and (2) EDTA after SFE with CO_2

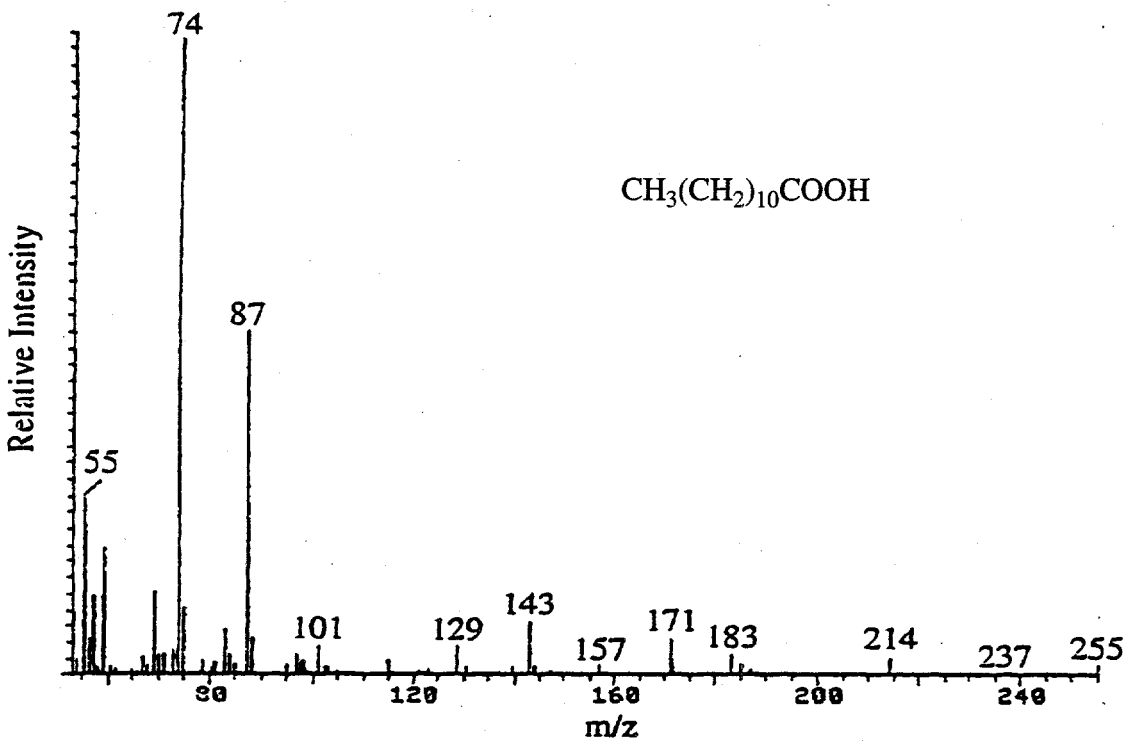


Figure 3.22. Mass Spectrum of Derivatized Lauric Acid

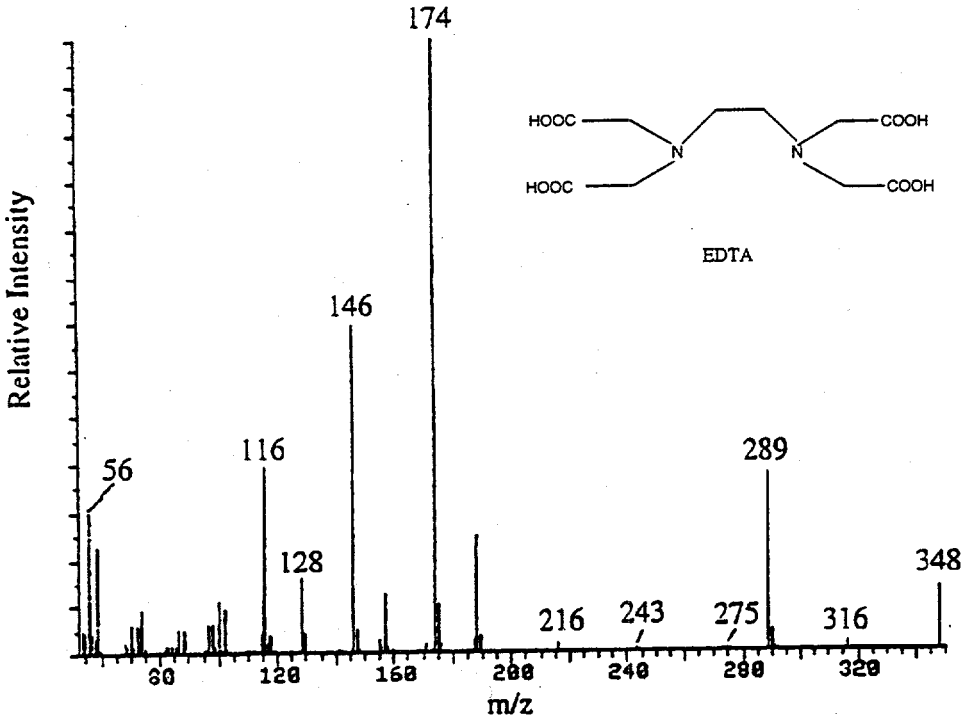


Figure 3.23. Mass Spectrum of Derivatized EDTA

to assume that this technique can be applied to SFE work as well. In addition to chelator analysis, it may also be possible to develop SFE conditions that will remove metal complexes intact for subsequent analysis.

3.5 Capillary Electrophoresis

Capillary electrophoresis (CE) is a rapidly growing separation technique. One of the greatest advantages is its diverse application range. Originally considered primarily for the analysis of biological macromolecules, it has proved useful for separations of compounds such as amino acids, chiral drugs, vitamins, pesticides, inorganic ions, organic acids, dyes, surfactants, peptides and proteins, carbohydrates, oligonucleotides and DNA restriction fragments, and even whole cells and virus particles.

Separation by electrophoresis is obtained by differential migration of solutes in an electric field. Capillary electrophoresis is performed in narrow-bore capillaries, typically 25- to 75 μm inner diameter (id), which are usually filled only with buffer. The mechanisms responsible for separation in CE are different from those in chromatography, and thus can offer orthogonal, complementary analyses. In addition, CE may offer simpler method development, minimal sample volume requirements, and lack of organic waste. Use of the capillary has numerous advantages, particularly with respect to the detrimental effects of Joule heating. The high electrical resistance of the capillary enables the application of very high electrical fields (100 to 500 V/cm) with only minimal heat generation. Moreover, the large surface area-to-volume ratio of the capillary efficiently dissipates the heat that is generated. The use of the high electrical fields results in short analysis times, high efficiency, and resolution. Peak efficiency, often in excess of 10^5 theoretical plates, is due in part to the plug profile of the electro-osmotic flow, an electrophoretic phenomenon that generates the bulk flow of solution within the capillary. This flow also enables the simultaneous analysis of all solutes, regardless of charge. In addition, the numerous separation modes that offer different separation mechanisms and selectivities, minimal sample volume requirements (1 to 10 nL), on-capillary detection, and the potential for quantitative analysis and automation, CE is rapidly becoming a premier separation technique.

One key feature of CE is the overall simplicity of the instrumentation. A schematic diagram of a generic capillary electrophoresis system is shown in Figure 3.24. Briefly, the ends of a narrow-bore, fused silica capillary are placed in buffer reservoirs. The content of the reservoirs is identical to that within the capillary. The reservoirs also contain the electrodes used to make electrical contact between the high-voltage power supply and capillary. The sample is loaded onto the capillary by replacing one of the reservoirs, usually at the anode, with a sample reservoir and applying either an electrical field or an external pressure. After replacing the buffer reservoir, the electrical field is applied and the separation performed. Optical detection can be made at the opposite end, directly through the capillary wall.

Figure 3.25 illustrates a CE separation for an over-the-counter cold medication. Peak 1 was phenylpropanolamine, peak 2- phenesphrine, and peak 3- dextromethorphan. The presence of dextromethorphan is of practical interest, since this material spends all of its time in the SDS micelle. Therefore, this component marks the practical end of the CE micellar separation. Preliminary results are shown in Figure 3.26. for the separation of NTA and EDTA. In addition, Figure 3.27. shows the separation of Sr- and Fe -EDTA complexes.

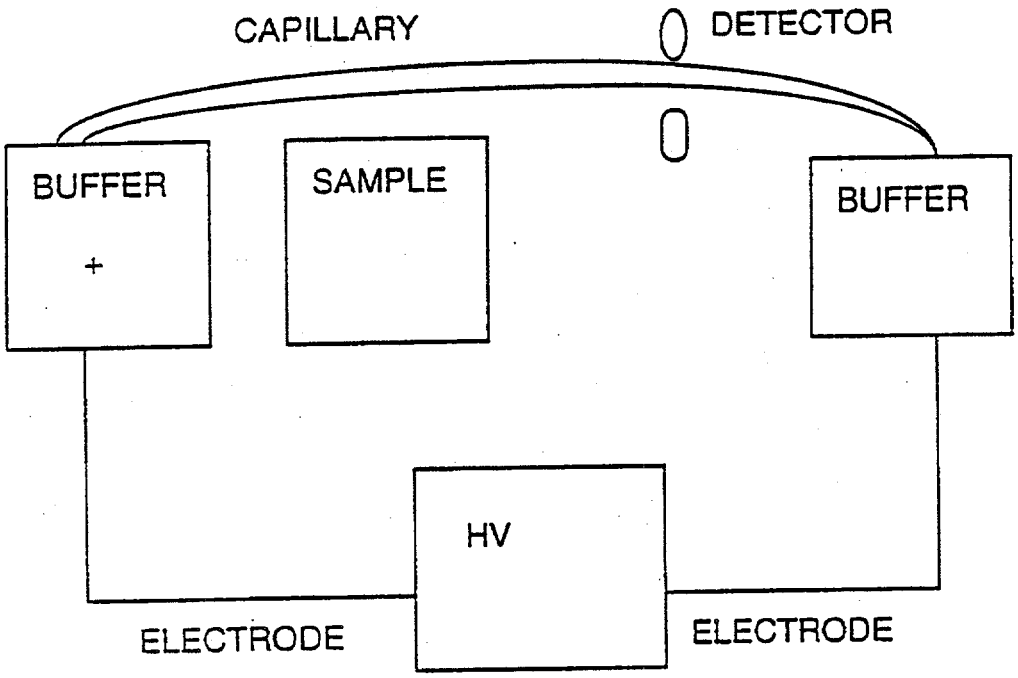


Figure 3.24. Schematic CE Instrumentation

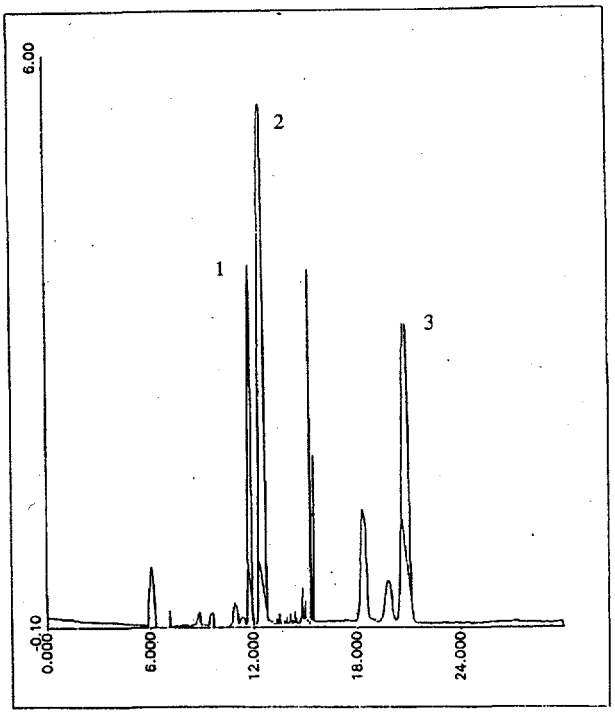


Figure 3.25. CE Separation of Amines, Peaks are (1) phenylpropanolamine, (2) phenesphrine, and (3) dextromethorophan

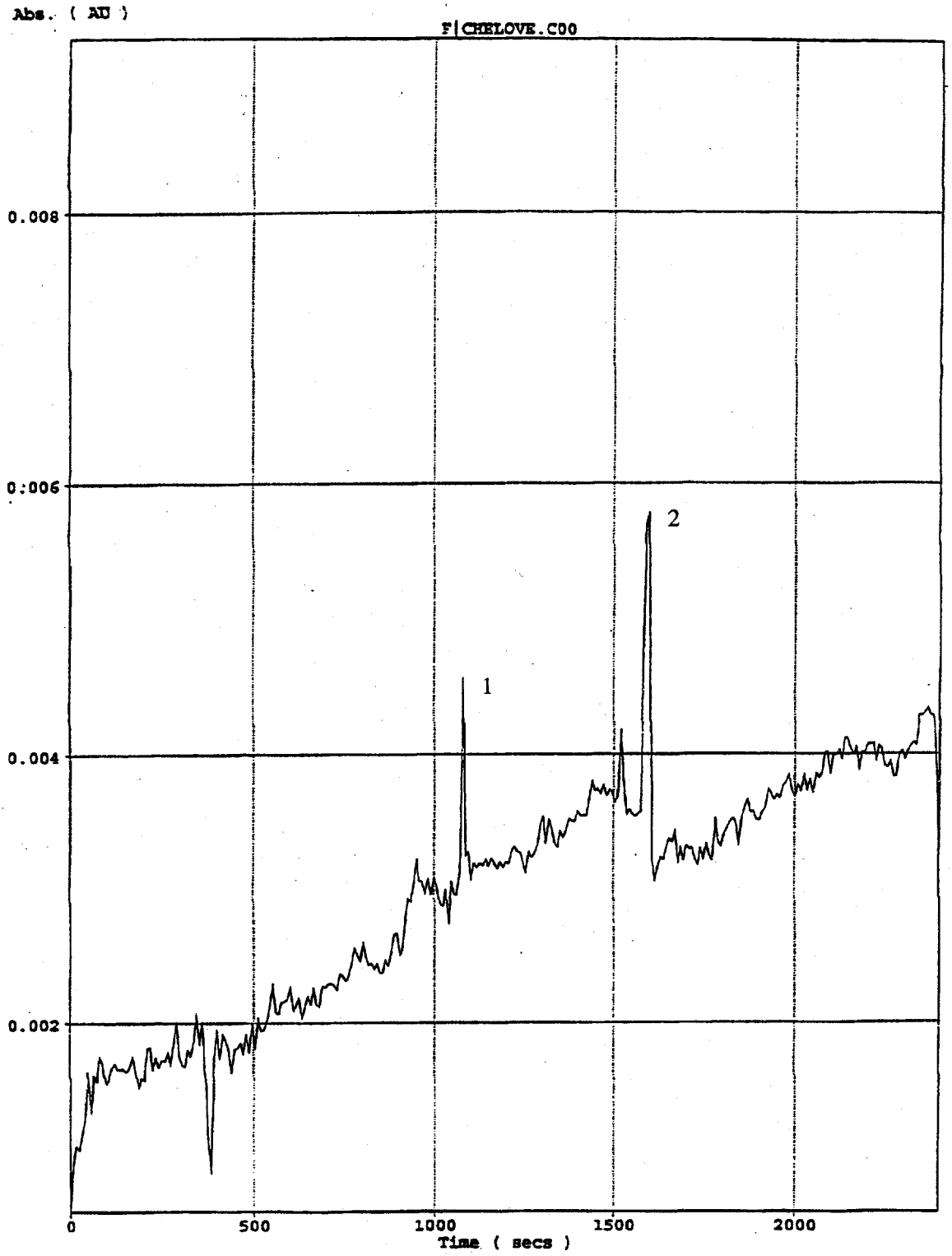


Figure 3.26. CE Separation of (1) NTA and (2) EDTA

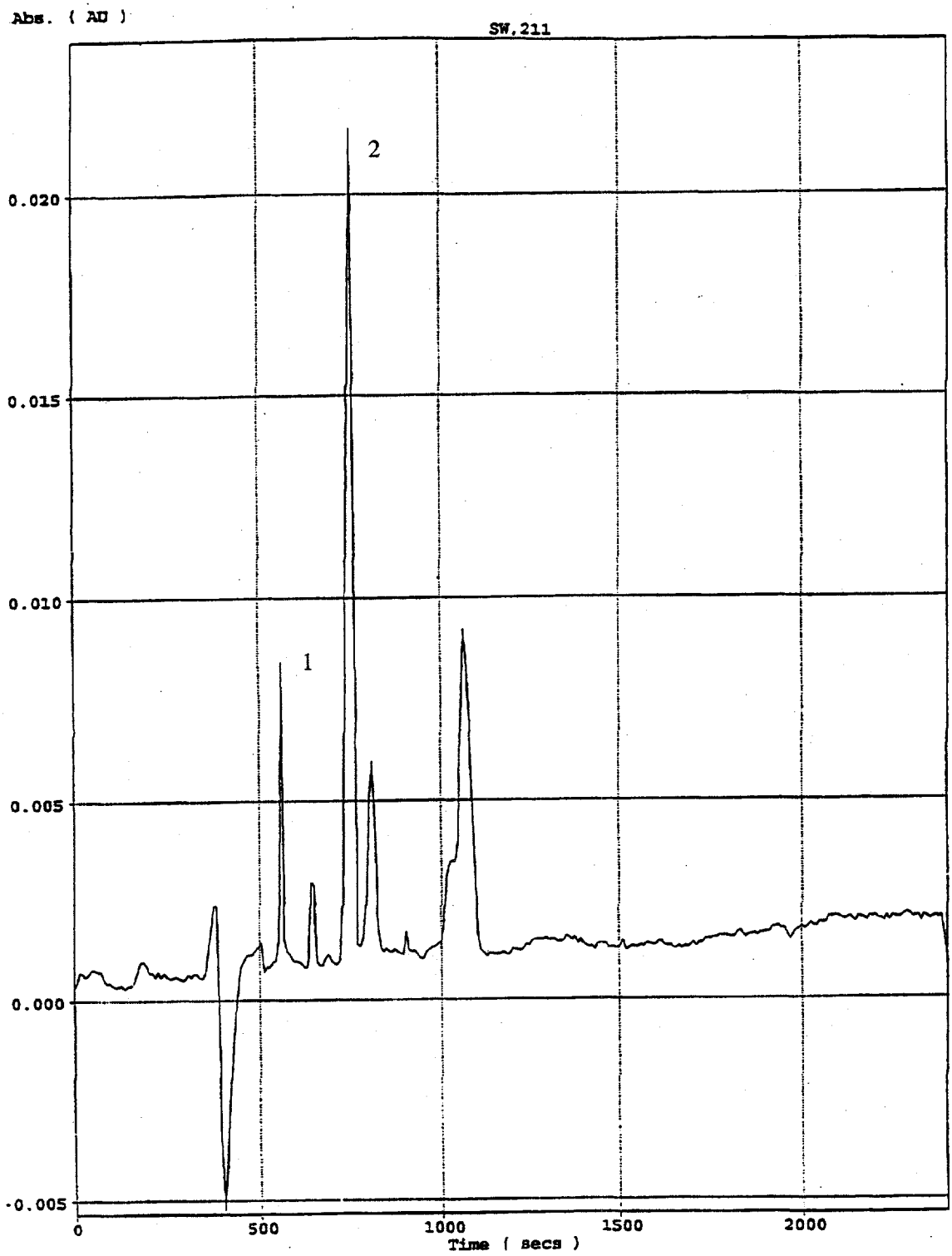


Figure 3.27. CE Separation of (1) Sr-EDTA and (2) Fe-EDTA

3.6 Analysis of Tank C-103 Samples

3.6.1 GC/MS Analysis of Liquid Organic Samples

Each of four organic layer samples was diluted by 10,000X with methylene chloride and analyzed by GC/MS. A standard of NPH was obtained from WHC. Standards of TBP (Aldrich) and dibutyl butylphosphonate (DBBP) (Pfalz and Bauer) were obtained.

The GC/MS instrument was equipped with a Hewlett Packard (HP) 5980 gas chromatograph (GC) operated in the splitless mode. A fused silica column (DB-5, 30m X 0.25 mm i.d., 0.25 μm film thickness, J & W Scientific, Folsom, CA) was used. The oven temperature was typically programmed in the following manner: 50°C for 1 min, 8°C/min to 300°C, and hold at 300°C for 5 min. The mass spectrometer (MS) was tuned daily with perfluorotributylamine (PFTBA). In these studies, the MS was scanned from 50 to 500 amu and operated in the electron impact mode (70 eV). The source temperature was 200°C, the injector port temperature was 250°C, and the interfaces were also at 250°C.

Chemical ionization MS was carried out with isobutane in the positive chemical ionization mode to obtain molecular weight information. The temperature of the source for positive ion chemical ionization mass spectrometry was 200°C. The MS was scanned from 70 to 500 amu in the positive ion mode.

Accurate mass measurements were performed on a JEOL SX 102/SX 102 high resolution mass spectrometer (HRMS). The instrument was tuned to a resolution of 5000 (10% valley definition). Data were acquired by scanning the magnetic field over the range of 10 to 600 according to procedure listed in the instructions. Instrument tuning and real-time mass measurements were performed by leaking perfluorokerosene into the electron impact ion source from the septum inlet reservoir. Computer-assisted accurate mass assignments and subsequent elemental compositions were made on data obtained from averaging four consecutive scans over the gas chromatographic elution profile of the analyte. The instrument was equipped with a HP 5980 GC. The GC was fitted with 30 m X 0.25 mm i.d. DB-5 capillary column (J & W Scientific). The GC oven temperature was held at 50°C for two min, then programmed at 5°C/min to 250°C. Scanning was initiated after a 5 min delay.

3.6.2 Analysis of Organic Layer

Table 3.1. lists the tentative identifications of components in the organic layer, their retention times (RT), and the absolute and relative weight-percent of each component. A total ion chromatogram is shown in Figure 3.28. Similar total ion chromatograms were obtained for all four organic layer samples.

The tentative identifications were based on the similarity of the mass spectrum of the component with the mass spectrum found in a data base or by manual interpretation. Confirmed identifications have been assigned based on comparison of mass spectra and GC retention times of the unknown component with authentic standard compounds. The identity of DBBP was confirmed by using the JEOL SX 102/SX 102 high resolution mass spectrometer. Figure 3.29 is a mass spectrum of DBBP. The fragment ion m/z 195 is $C_6H_{20}O_3P$ as determined by high resolution mass spectrometry (accurate mass measurements)with the following structure, where Bu is a butyl group:

Table 3.1. Components Determined from GC/MS Analysis of Organic Layer of Tank C-103

Component	RT	Weight %	Relative Wt %
dodecane	10.51	2.8	3.8
alkane	10.74	0.2	0.3
alkane	11.85	1.1	1.5
tridecane	12.38	11.4	15.5
alkane	13.23	0.5	0.6
alkane	13.72	1.0	1.3
tetradecane	14.17	6.0	8.1
alkane	15.17	0.7	1.0
pentadecane	15.84	0.9	1.2
DBBP	17.60	1.9	2.6
TBP	18.09	47.2	64.0
Total		73.7	100.0

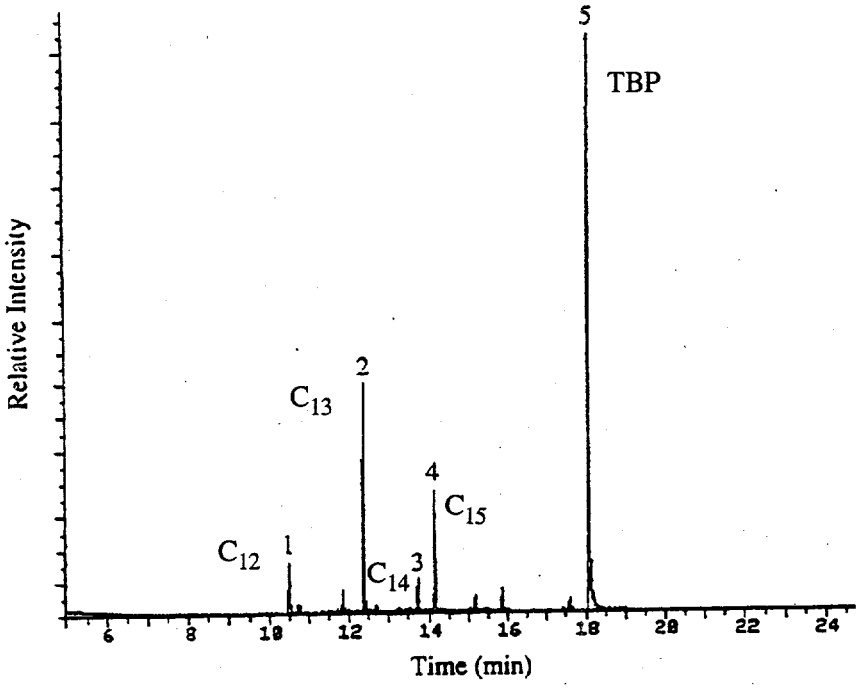


Figure 3.28. Total Ion Chromatogram of Organic Layer Sample from Tank C-103

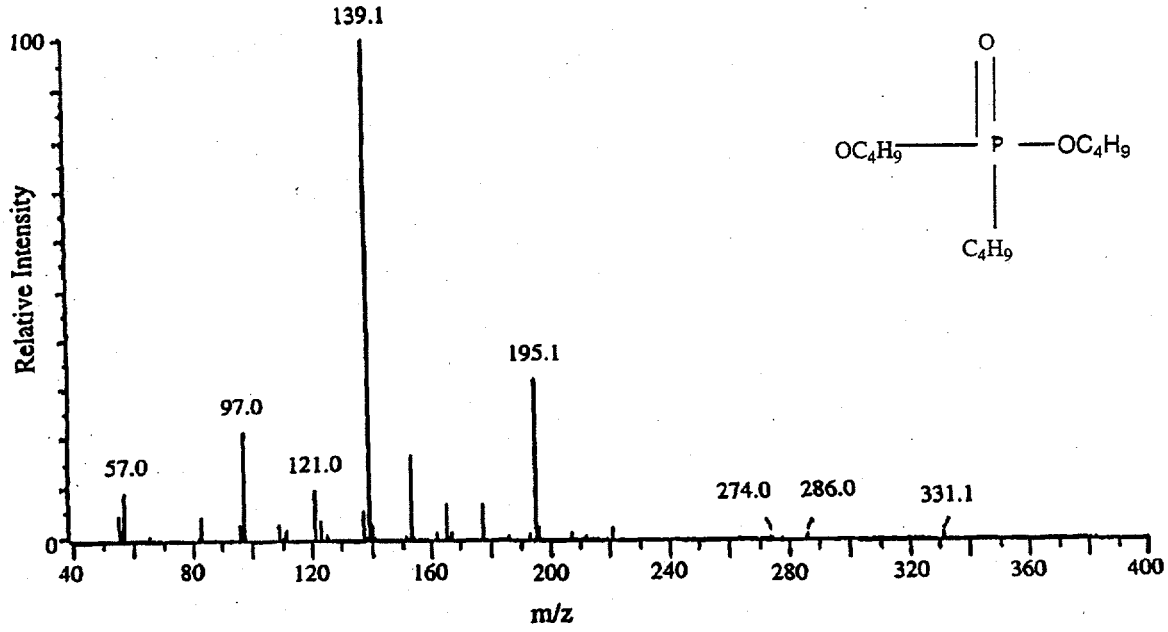
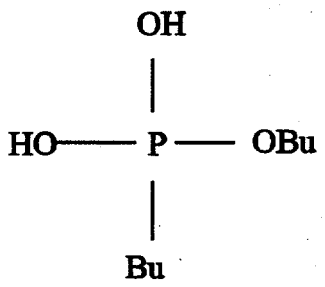
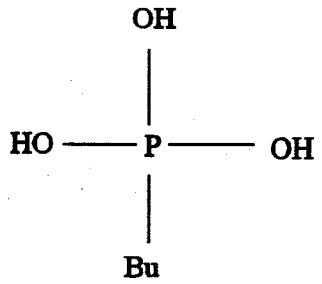


Figure 3.29. Mass Spectrum of DBBP



The fragment ion m/z 139 is $C_4H_{12}O_3P$ with the following structure:



The semivolatiles found in the organic layer of Tank C-103 are primarily TBP and related phosphate esters, a series of n-alkanes (undecane through pentadecane), and several branched-chain alkanes. It is very difficult to determine the exact structures of branched alkanes, primarily due to the lack of molecular weight information (nonexistent or weak parent ion). The electron impact mass spectrum of most alkanes are practically identical.

The relative weight ratio of TBP:NPH is 67:33, if DBBP is included in with the TBP, and the branched alkanes were included with NPH. Tributyl phosphate constitutes 48.3% by volume of the organic layer. In addition, in analyzing a weighed sample, approximately 74% of the organic carbon could be accounted for.

A weighed sample of the organic layer was heated to 320° C for 15 min under vacuum (2x10-6 torr) using a direct probe. The results indicate that 10-20% of the material by weight was volatilized at 320° C. However, direct probe analysis of a mixture of TBP and NPH showed no remaining residue. In addition, direct probe analysis under chemical ionization conditions showed ions a m/z 267 and 534; these ions are attributed to TBP. A diluted sample of the organic layer was also analyzed by GC/MS using a thick film column. No lower molecular weight material was observed. The residue remaining in the capillary tubes from direct probe analysis was heated to approximately 600 and 1000° C in a carbon analyzer. The total carbon value at 600° C was determined to be 2.9 mg C. A 5-μL sample weights 4.4 mg assuming a density of 0,88 mg/L. The quantity of carbon is then 66%. From the results of the analysis of the organic layer and assuming TBP is approximately 50% and NPH constitutes 25%, only 47% of the organic carbon is accounted for by NPH and TBP. Additional derivatization experiments for the analysis of chelators indicated no detectable chelator species. Therefore, there is a portion of the organic cabon that is not detected.

A 5-μL sample of the original organic layer was also heated to 600° C and then subsequently heated to 1000° C in a carbon analyzer. No additional total organic carbon was detected. These results indicate that most of the organic carbon has been volatilized at a temperature of approximately 320° C under vacuum. The remaining residue left after heating to 320° C was analyzed by scanning electron microscopy (SEM). Examples of the electron micrographs are illustrated in Figures 3.30 and 3.31. Inorganic phases that were tentatively identified include $K_2Ca_2Mg(SO_4)_4$, $KAlSi_3O_8$, $Ca_3(PO_4)_2$, FeOOH-CrOOH, and AlOOH. These phases are probably not soluble in the organic phase, but may exist as colloidal particles. A l-mL aliquot of the organic layer was heated overnight at 300° C in a muffle furnace; the remaining residue was examined using X-ray fluorescence (XRF). The elemental determinations on the radioactive sample must be considered as semiquantitative due to inadequate sample transfer. However, the major components detected were Si (8950 ppm) and P (75,100 ppm). Minor components detected included S, Ni, Ca, Cr, and Ti.

3.6.3 Analysis of Organic Layer Headspace

Aliquots (1 mL and 100 μL) of one of the organic phase samples were placed in 20-mL headspace vials. Headspace analyses were performed with a HP 7694 Headspace Sampler interfaced to a HP 5890 GC equipped with a DB 624 (30 M X 0.53 mm and 3 μm film thickness) and a flame ionization detector. A sample was heated to 40°C $\pm$ 3°, equilibrated for 10 min, and analyzed. The sample was then heated and analyzed at 70° $\pm$ 3°C and 100° $\pm$ 3°C. A 500 μL sample from the headspace of the sample heated to 40°, 70°, and 100°C was taken with a gas-tight syringe (10 mL) which also had been heated to the related temperatures, and analyzed using a HP Mass Selective Detector equipped with a

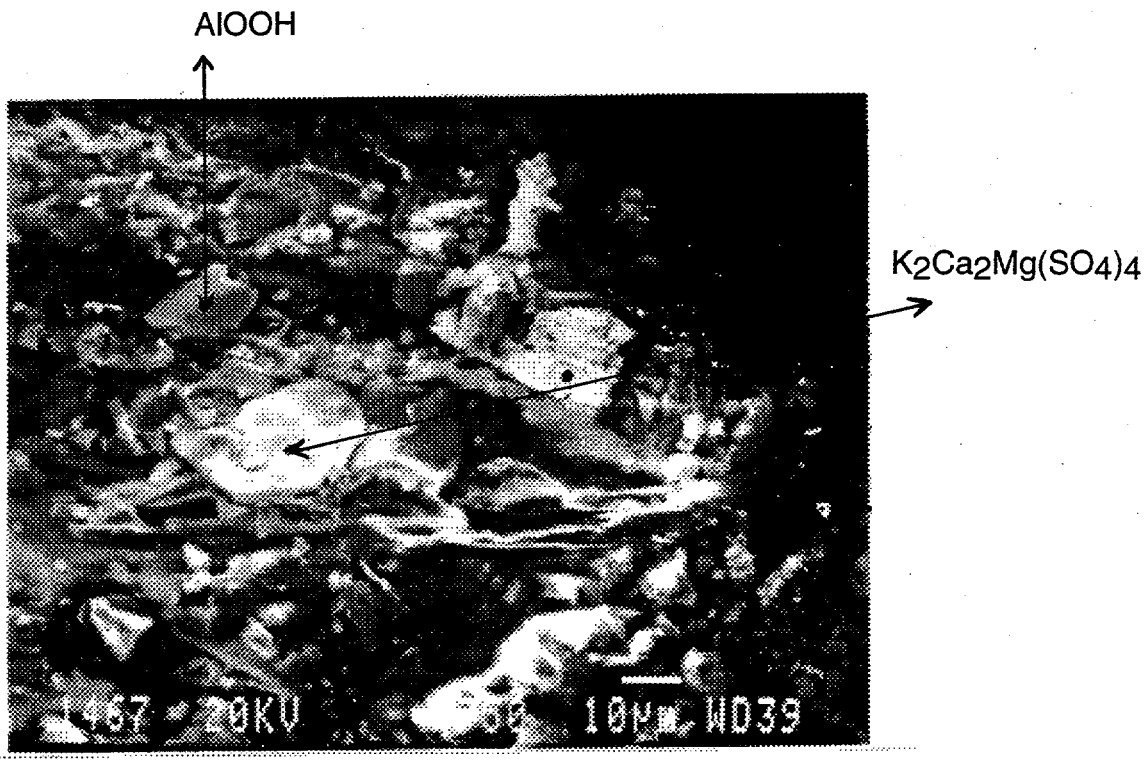


Figure 3.30. Electron Micrograph of Residue (Section 1)

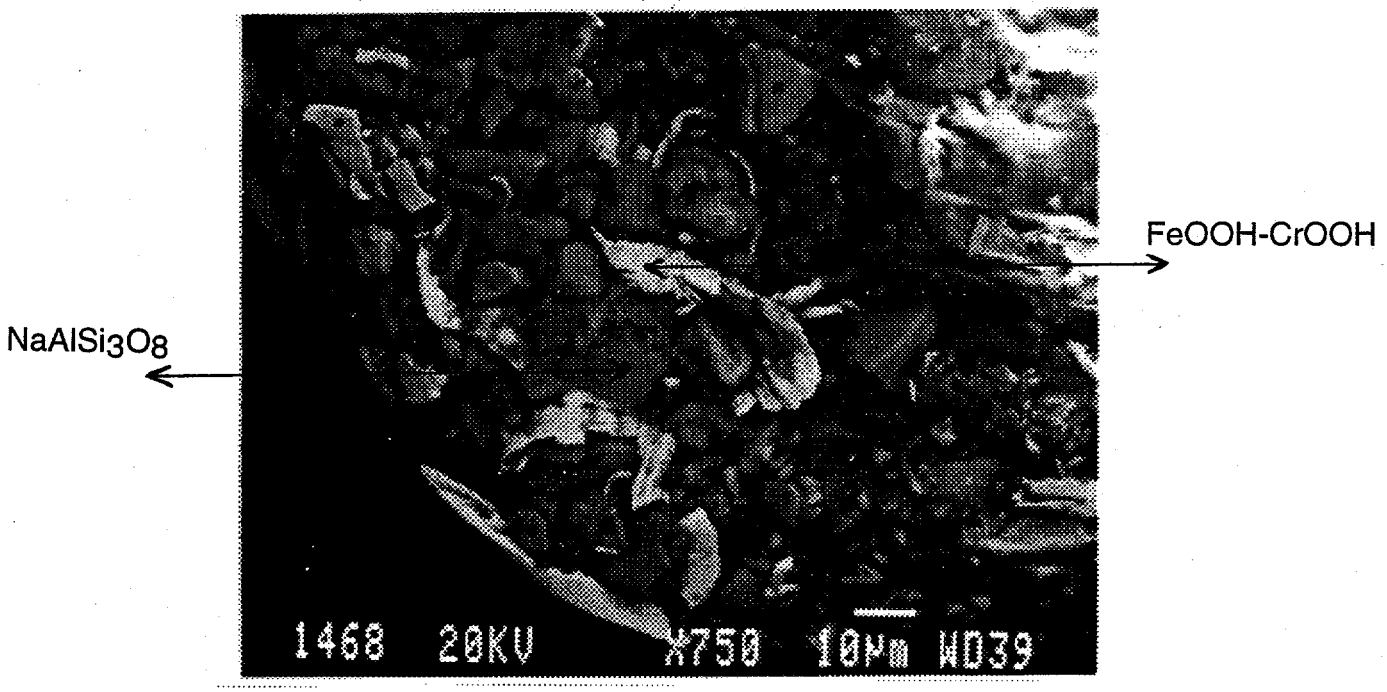


Figure 3.31. Electron Micrograph of Residue (Section 2)

DB-5MS (30 M X 0.25mm and 0.25 μm film thickness). Due to radioactivity levels, 50 μL of the aqueous phase was placed in a 20 mL headspace vial, 50 μL of distilled water was added, and analyzed using the above-mentioned procedure. In addition, the headspace samples were also analyzed using MS.

The estimated concentrations of the components at 40°, 70°, and 100°C are listed in Table 3.2. The tentative identifications of the components are based on mass spectral interpretation and best match with the mass spectral library. The concentrations are based on the response factor for a 50 ppm liquid sample of tridecane. The detection limit was .01 mL. The peaks were normalized to the one of highest concentration. As a result the concentration of these components near the detection limits at 70°C, were below the detection limit at 100°C.

Table 3.2. Determined Concentrations of Tentatively Identified Components (mg/L) in Headspace Analysis of Organic Fraction

Component	Retention Time, Min.	40°C	70°C	100°C
pentanenitrile	7.494	-	0.01	-
ketone	7.983	-	0.02	-
alkane	8.461	-	0.01	-
ketone	10.206	-	0.01	-
heptanenitrile	10.923	-	0.02	-
branched alkane	11.235	-	0.01	-
decane	11.525	-	0.02	-
alkane	11.609	-	0.01	-
branched alkane	12.087	-	0.01	-
octanenitrile	13.459	-	0.01	-
undecane	13.887	0.06	0.22	1.46
branched alkane	15.031	-	0.06	-
branched alkane	15.250	-	0.03	-
branched alkane	15.375	-	0.02	
alkane	15.75	-	0.07	
ketone	15.769	-	-	0.76
dodecane	15.95	0.32	2.4	13.8
alkane	16.185	0.05	0.32	2.2
alkane	16.77	-	0.13	
alkane	17.28	0.08	0.62	3.6
alkane	17.662		-	0.12
tridecane	17.87	0.46	4.2	18.2
alkane	18.101	-	0.10	
alkane	19.09	0.07	0.36	0.64
tetradecane	19.51	0.22	1.2	6.4
alkane	20.47	0.03	0.11	0.68
pentadecane	21.10	0.02	0.12	0.70
DBBP	22.72	0.01	0.04	0.58
TBP	23.20	0.14	0.78	8.4

At 40°C, the major components are NPH-related, but there is a minor contribution from TBP. The component at a retention time of 22.724 min is DBBP. At 70°C, there are nitrile compounds tentatively identified. These include pentanedinitrile, heptanenitrile, and octanenitrile. The estimated concentrations for NPH are higher than for TBP. In addition, several ketones and alkane-related components were also tentatively identified. The estimated concentrations of NPH are much higher than TBP at 100°C.

At 40°C, the sum of the NPH-related components amounts to 1.32 mg/L, which is comparable to the analysis (range 0.55 to 1.31 mg/L) performed on the headspace in the tank.

3.6.4 Solvent Extraction of Aqueous Layer and Analysis Using GC/MS

A 5-mL aliquot of the aqueous layer was combined with 5 mL of doubly-distilled water and extracted 3 times with equal 10-mL volumes of methylene chloride. This procedure was done in duplicate. The methylene chloride fractions were combined and passed through a column of sodium sulfate. The volume of methylene chloride was reduced to 1 mL. The sample of aqueous layer was acidified and extracted 3 times with equal 10-mL volumes of methylene chloride. The methylene chloride volume was reduced to 1 mL. Both the acid and base-neutral extracts were then analyzed by GC/MS.

The results of GC/MS analysis of the base-neutral fractions show that DBBP and TBP were the major components. The average concentration of DBBP was found to be 7 μg/mL, and the average concentration of TBP was 80 μg/mL. The percent difference for duplicate samples was approximately 10%. Normal paraffin hydrocarbon was found just above the detection levels. Concentration of NPH was estimated to be 1 to 3 μg/mL. No additional components were detected in the acid fraction.

3.6.5 Headspace Analysis by GC/MS

Due to radioactivity limits of the 325 laboratory, only 40 μL of the aqueous sample could be placed in a 2-mL headspace vial. Table 3.3 lists the concentrations of the components in the headspace of the aqueous layer at 40°, 70°, and 100°C.

Due to the large headspace volume to sample size (20 mL and 50 mL), the results may reflect concentrations in the liquid and not in the headspace. As a result, experiments are underway to use a 2 mL headspace vial. The total ion chromatogram obtained at 70°C is very similar to that obtained at 100°C. The spectra are predominantly NPH, NPH-related components, and TBP.

Table 3.3. Determined Concentrations (mg/L) of Components in Headspace of Aqueous Phase

Component	40°C	70°C	100°C
Tridecane	0.001	0.002	0.02
Tetradecane	0.001	0.01	0.01
DBBP		0.002	0.01
TBP	0.004	0.07	0.24

3.7 Mass Spectrometry

The JEOL tandem high resolution mass spectrometer (HRMS) has been an invaluable analytical tool for the analysis of tank waste. It has been utilized to identify derivatized components in waste from Tank 101-SY. In addition, it has been used to identify components in the organic layer from Tank C-103. Dibutyl butyl phosphorate was one component unambiguously identified in the floating organic layer. The structure of the synthesized deuterated EDTA (for use on recovery studies under the Flammable Gas Safety Program) and purity were confirmed using HRMS.

The instrument has also been for analytical methods development, primarily electrospray ionization. This technique will allow the direct analysis of waste without derivatization.

3.8 High Temperature Extraction of 101-SY Samples

At the beginning of FY 1993, only approximately 10-20% of the water soluble organic carbon could be accounted for by derivatization gas chromatography/mass spectrometry (GC/MS) and liquid chromatography (LC). All of the sample preparation including derivatization for chelator analysis was performed in the hot cell facilities. Typically, a 5-g waste sample was stirred with 10 mL of doubly-distilled water overnight at room temperature. The solution was filtered through a 0.45 μm filter to remove any solid material. The aqueous solution was then dried using nitrogen-blow-down techniques, and the remaining residue was then heated with 2 mL of boron trifluoride/methanol for 1 h at 100° C to produce the methyl esters of chelators, chelator fragments, and carboxylic acids. After the solution cooled to room temperature, 1 mL of chloroform was added to the solution and the entire mixture was added to 3-5 mL of KH_2PO_4 adjusted to pH 7.0 with NaOH. The organic layer containing the methyl esters was separated and subsequently analyzed using gas chromatography/mass spectrometry (GC/MS).

It was hypothesized that one of the problems with poor TOC accountability was due to the incomplete water solubilization of the organic carbon. Experiments were designed to increase the amount of water-soluble organic carbon; extraction at elevated temperatures was performed. A 2-g sample of the convective layer from Tank 101-SY was heated in the hot cell facility to approximately 50° C in 10 mL of doubly-distilled water while stirring. The amount of gas evolution was so large that the vial would not remain capped; the solution also foamed and resulted in spillage of the sample in the hot cell. The experiment was repeated with a smaller waste sample from the convective layer, but the results were the same. No quantitative TOC data could be obtained; the amount of entrained gas bubbles precluded obtaining any TOC data. The same procedure was performed with a sample of the nonconvective layer, and no gas evolution was observed.

To determine the organically-soluble carbon, chloroform extracts of the core composite samples were analyzed using GC/MS. The results are shown in Table 3.4. The concentration of NPH is highest in sample R4258; the results from TOC studies indicate the presence of water insoluble organic carbon. Table 3.5 shows the TOC accounted for by chelators, chelator fragments, NPH, and low molecular weight carboxylic acids (Campbell et al. 1994).

In summary, the increase in TOC accountability was not a function of high temperature extraction. On the contrary, the increase in TOC accountability was due to reducing the radioactivity levels in

waste samples using cation exchange resin so that the samples could be removed from the hot cell. This allowed the critical parameters of heat and dryness of sample involved in the derivatization procedure to be more easily controlled. In addition, determining the amount of NPH contributed to TOC accountability. Due to gas evolution from entrained bubbles released during heating, the high temperature extraction procedure was not successful with samples of the convective layer. In view of the fact that 73-93% of the TOC can be accounted for in samples from SY-101, very little, if any, water soluble carbon remains unidentified.

High temperature extraction for increasing the water-extractable carbon may be applicable to waste samples where gas evolution is not a problem. Other extraction procedures are also being explored. Continuous or repetitive extractions, if TOC accountability is low, will be considered when other waste samples become available. In addition, recently, preliminary work has been done to determine the feasibility of extracting chelators from a complex matrix by supercritical fluid extraction (SFE). The difficulty is that the chelators are highly polar and as such are not amenable to SFE extraction even with a polar modifier like methanol. Several groups that have researched the extraction of acids from a complex media by SFE have successfully used *in situ* SFE methylation or silylation to reduce the polarity of the acids. This involves adding the appropriate derivatizing reagent to the matrix and then using supercritical fluid that has been modified with the commonly used derivatizing solvent. This approach has been applied to ethylenediaminetetraacetic acid (EDTA) and iminodiacetic acid (IDA) in sand matrix using BF_3/methanol and was found to be successful. Work is now being done to refine this approach. If successful with tank wastes, the stability and lifetime of the derivatives may be increased. In addition, an approach to add BF_3/methanol as a modifier will also be investigated.

3.9 Use of Cation Exchange for Radioactive Level Reduction

Although the use of cation exchange for the reduction of radioactivity levels to remove the waste samples from the hot cell and perform derivatization in a fume hood was initiated under the Flammable Gas Safety Program, a letter report was submitted under the auspices of the Organics Tanks Safety Program describing the results from studies on the sodium form of the cation exchange material.

Table 3.4. Concentration (ppm) of Normal Paraffin Hydrocarbon (NPH) in Tank 101-SY Core Segment Samples

Sample	Segment #	NPH
R4258	4	1440
R4259[(a)]	6	
R4260	9	410
R4261	11	670
R4262	16	20
R4263[(a)]	17	

(a) Insufficient sample remaining to determine concentration of NPH.

Table 3.5. Total Organic Carbon (TOC) Accounted for by Chelators, Chelator Fragments, Low Molecular Weight Acids, and Normal Paraffin Hydrocarbon (NPH) in Tank 101-SY Window E Core Segment Samples (mg C/g sample)

Sample[(a)]	Segment #	Chelators[(b)]	Low Molecular Weight Acids[(c)]	% TOC Accounted For
R4258/C	4	4.7 (44%)[(d)]	3.3 (30%)	74(87)[(e)]
R4259/C	6	3.3 (33%)	4.5 (44%)	77
R4260/C	9	4.8 (46%)	4.4 (41%)	87(91)
R4261/C	11	6.4 (52%)	2.5 (23%)	75(81)
R4262/NC	16	2.2 (20%)	5.8 (53%)	73
R4263/NC	17	3.6 (32%)	6.8 (61%)	93

(a) Sample R4264, a nonconvective layer sample, was lost during preparation; the analysis is in progress.
(b) Includes chelators, chelator fragments, nitrosated chelator material, and several carboxylic acids.
(c) Low molecular weight acids include acetic, glycolic, oxalic, and formic.
(d) Parentheses give percent of TOC accounted for by analyte category.
(e) Percent in parentheses includes NPH.

C Convective layer
NC Nonconvective layer

All of the sample preparation including derivatization for chelator analysis was performed in the hot cell facilities in FY 1993. Typically, a 5-g waste sample was stirred with 10 mL of doubly-distilled water overnight at 25°C. The solution was filtered through a 0.45 μm filter to remove any solid material. The aqueous solution was then dried using nitrogen-blow-down techniques, and the remaining residue was then heated with 2 mL of boron trifluoride/methanol for 1 h at 100° C to produce the methyl esters of chelators, chelator fragments, and carboxylic acids. After the solution cooled to room temperature, 1 mL of chloroform was added to the solution and the entire mixture was added to 3-5 mL of KH_2PO_4 adjusted to pH 7.0 with NaOH. The organic layer containing the methyl esters was separated and subsequently analyzed using gas chromatography/mass spectrometry (GC/MS). At that point, only 10-20% of the total organic carbon (TOC) could be accounted for.

Parameters essential for good recoveries from the derivatization procedure with tank waste samples are not easily controlled through the use of remote manipulators in the hot cell facilities. The dryness of the sample is critical to obtaining reproducible results from derivatization using BF_3/methanol. This parameter and monitoring the heating of the sample during derivatization are parameters that are not easily controlled with sample preparation in the hot cell. The 101-SY matrix is laden with hygroscopic salts, which tend to crust over and encapsulate water in the drying process. Manipulation of the sample (outside of the hot cell in a fume hood) would allow sample monitoring and effective removal of residual water. However, in order to remove the samples from the hot cell, the radioactivity levels would

have to be dramatically reduced. As a result, it was extremely important to develop a method for reducing the radioactivity levels without removing or introducing any organic carbon. In view of the fact that many of the suspected radioactive contaminants were cationic in nature, the use of cation exchange for the reduction of radioactivity was suggested.

The possible use of the cation exchange material for radioactivity removal was substantiated during a liquid chromatographic analysis of a tank waste sample. A 1-mL aliquot of the water extract from a Tank 101-SY composite sample was diluted and analyzed using liquid chromatography in a radioactive zone. After the analysis was complete, a counter was used to check for radioactive contamination. The LC column was scanned, and most of the radioactivity was located within the guard column consisting of cation exchange packing material. A guard column is used prior to the analytical column to collect contaminants. As a result, a step involving cation exchange to remove the radioactivity was added to the separation procedure. The use of cation exchange resin to remove the radioactivity allowed the samples to be removed from the hot cell to a fume hood; this was probably the single most important step in controlling the dryness of the sample prior to derivatization and heating during the derivatization procedure which subsequently increased the TOC accounted for.

Initial tests were then performed to determine any losses of HEDTA and EDTA going through the Na^+ form of the cation exchange column. Preliminary results indicate the recoveries were approximately 90 and 95%, respectively. Further studies are underway to substantiate these numbers. However, if one uses the hydrogen form of the resin, losses of EDTA do occur, presumably due to insolubility of the acid form of EDTA.

The presently accepted sample preparation for analysis of core samples of 101-SY for organics is as follows. The TOC of an aliquot is determined on the starting material. A 5-g sample is stirred with 10 mL of doubly-distilled water overnight. The solution is then filtered through a 0.45 μm filter. The TOC is measured on the remaining solid material. The filtered solution is then passed through a preconditioned-Dowex 50 AGX cation exchange resin (Na^+ form, 10 g) and then rinsed with approximately 10 mL of an alkaline solution water to ensure no organic carbon is left on the column. The radioactivity level of the resulting solution is approximately 200 times less than the original sample. This allows us to remove the aqueous sample from the hot cell to perform the derivatizations in the fume hood. The TOC was not changed by passing through the cation exchange column. The material was analyzed for radionuclides after passing through the cation exchange column, and the results indicate it is primarily cesium. However, with the techniques used (Gamma Energy Analysis), Sr would not have been detected. Further studies are underway to determine the identity of radioactive analytes removed. Transferring the derivatization procedure to the fume hood has improved our reproducibility and allows control of the parameters crucial to reproducible results, temperature and dryness of the sample. The results of TOC accountability from Tank 101-SY core segment samples with incorporation of the cation exchange for radioactive removal are shown in Table 1.

To determine if any TOC losses occur through the cation exchange column, TOC values were determined before and after the cation exchange procedure with tank waste samples. In addition, blanks were also analyzed to determine if any TOC was introduced from the column. The results are shown in Table 2. These results clearly indicate that the cation exchange column (Na^+ form) does not remove or introduce any TOC. This is an extremely important aspect; the sample was not compromised by eluting through the cation exchange resin. Additional studies are underway to support these results.

The incorporation of the cation exchange step to remove radioactivity was certainly successful in the analysis of samples from Tank 101-SY. However, the assumption can not be made that it will work for every tank waste sample. As an example, the results from T-111 samples indicate the loss of carbon going through the cation exchange column. The question at this point is whether it is indeed organic carbon that is lost. The pH of the T-111 sample was 9; as a result, pH of the sample may be an important variable in using the exchange column for reduction of radioactivity. Further studies are underway to examine this phenomenon. It is recommended that the total organic carbon measurements be made prior to and after the cation exchange column to ensure the no TOC has been removed or added to the sample. In addition, it is also unreasonable to expect that 73-93% of the TOC can be accounted for in every waste sample.

The method of reducing the radioactivity level in tank waste samples has been transferred to the Analytical Chemistry Laboratory (ACL) and is the process of being transferred to the 222-S laboratory through Kim Wehner.

Other methods to separate the radioactive components from the organic constituents are also being explored. One difficulty is that the chelators are highly polar and as such are not amenable to SFE extraction even with a polar modifier like methanol. Several groups that have researched the extraction of acids from a complex media by SFE have successfully used *in situ* SFE methylation or silylation to reduce the polarity of the acids. This involves adding the appropriate derivatizing reagent to the matrix and then using supercritical fluid that has been modified with the commonly used derivatizing solvent. Preliminary results with a test matrix indicate that in situ derivatization followed by SFE provides adequate recoveries of analytes. The technique of derivatization followed by SFE will be extended to simulated wastes.

4.0 Methods Development Transfer

A method has been accepted to fully document methods development transfer. The method will be developed and transferred to designated personnel. A cover statement will be signed by both the transferor and the receiver. The test plan will then be developed, completed, and signed by the test plan author and technical group leader. The entire package, which includes the transferred method, cover statement, and test plan, will then be forwarded to the appropriate WHC project manager. Additional training and consultation will be provided if required.

Various methods have been transferred to personnel in the ACL and the laboratory at 222-S. The LC method for LMWA and the LC method for HEDTA and EDTA have been transferred to the personnel at the ACL and the laboratory at 222-S. These methods are being used by the ACL in the analysis of tank waste samples before grout treatment. The derivatization GC/MS methods and the LC/MS methods for chelators, chelator fragments, and LMWA have been transferred to the ACL during FY 1994. A transfer letter was signed on May 24, 1994 by Robert Stromatt of the ACL and a letter of transfer was signed by Kim Wehner of the 222-S laboratory on May 24, 1994. Further discussions are scheduled with Kim Wehner, WHC, for additional transfer of methods including GC/MS analysis of TBP and NPH for the samples scheduled to be obtained from Tank 102-C.

5.0 Future Work

The objective of this task is to develop analytical methods that can be used to identify and/or quantify the amount of particular organic functional species in Organic Tank wastes. This work will involve examining direct spectroscopic (UV, IR, Raman) methods as well as indirect methods such as dissolution followed by spectroscopic, chromatographic, or derivatization techniques for the elucidation of functional species.

Methods verification and transfer to the analytical laboratory will be required. Many current methods for analysis of organics are both time-consuming and expensive. The focus of this activity is to complete the documentation of the developed analytical methods, obtain the necessary reviews, approvals, and training required to have the methods adopted for routine analysis in the Analytical Chemistry Laboratory and 222-S personnel. In addition, as methods are developed for the direct analysis of waste samples for chelators, chelator fragments, and carboxylic acids, they will be transferred to the Flammable Gas Safety Program.

Methods will be sought that result in faster isolation and separation of organic constituents resulting in minimal sample handling and waste accumulation. Use of fast separation techniques such as microbore chromatography or CE, and specific detection devices that can be applied to poorly separated analytes will be investigated.

Methods for the quantitative analysis of chelators and chelator fragments not requiring derivatization will be examined, such as electrospray mass spectrometry and Matrix Assisted Laser Desorption Ionization (MALDI) - Time of Flight Mass Spectrometry (TOFMS). The MALDI instrumentation has the potential of analyzing chelators and chelator fragments and complexed chelators intact. The MALDI-TOF instrument would provide a capability for analyzing nonvolatile components in waste without derivatization.

6.0 References

Ashby, E. C., C. Jonah, D. Meisel, L. R. Peterson, and D. M. Strachan. 1992. *Gas Generation and Retention in Tank 241-SY-101: A Summary of Laboratory Studies, Tank Data, and Information Needs*, PNL-8124. Pacific Northwest Laboratory, Richland, Washington.

Brunner, E.; 1985. J. Chem. Thermodyn., 17: pp. 671-679.

Campbell, J. A. et al. 1994. *Flammable Gas Safety Program. Analytical Methods Development: FY 1993 Progress Report*, PNL-8042, Pacific Northwest Laboratory, Richland, Washington.

Campbell, J. A. 1994. *TOC Accountability*. Letter Report to Dave Turner, WHC Manager of Organics Tanks Safety Program.

Campbell, J. A. et al. 1992. *Characterization of Coal-Derived Materials by Field Desorption Mass Spectrometry, Two-Dimensional Nuclear Magnetic Resonance, Supercritical Fluid Extraction, and Supercritical Fluid Chromatography/Mass Spectrometry*. PNL-8224, Pacific Northwest Laboratory, Richland, Washington.

Campbell, J. A. et al. 1994. *Flammable Gas Safety Program. Analytical Methods Development: FY 1993 Progress*. PNL-9062, Pacific Northwest Laboratory, Richland, Washington.

David, F., Verschuere, M., and Sandra, P. 1992. Fresenuius Journal of Analytical Chemistry, 344(10-11), pp. 479 - 485.

Edmonds, C. G. and R. D. Smith. 1990. Methods in Enzymology, 193:412-431.

Field, J. A. et al. 1992. Anal. Chem. 64(24), pp. 3161 -3167.

Gitterman, M. and Procaccia, I. 1983. J. Chem. Phys., 78:2648-2654.

Griffiths, P. R. and J. A. deHaseth. 1986. *Fourier Transform Infrared Spectroscopy, Chemical Analysis*. Vol. 83, pp. 564-610, John Wiley and Sons.

Hawthorne, S. B., et al. 1992. Anal. Chem., 64(4), pp. 405-412.

Hills, J. W., Hill, H.H., Maeda, T. 1991. Anal. Chem., 63(19), pp. 2152-2155.

HP 7680A Supercritical Fluid Extractor Manual, "Preparing Samples by Supercritical Fluid Extraction", (Manual P/N 07680-90330), pp. 2-7 (1990).

Huckaby, J. L. 1994. *Tank 241-C-103 Headspace Flammability*. WHC-EP-0734,Westinghouse Hanford Company, Richland, Washington.

Kebarle, P. and L. Tang. 1993. Anal. Chem. 65:972A-986A.

Klem, M. J. 1990. *Inventory of Chemicals Used at the Hanford Site Production Plants and Support Operations (194-1980).* WHC-EP-0172, Westinghouse Hanford Company, Richland, Washington.

Lee, H. B., Peart, T. E., and Hong-You, R. L. 1992. J. of Chromatography, 605(1), 109 -113.

Light-Wahl, K. J., B. L. Schwartz, and R. D. Smith. 1994. J. Amer. Chem. Soc. 116:5271-5278.

McHugh M. A. and Krukonis V. J. 1986. Supercritical Fluid Extraction, Principles and Practice. (Butterworth, Boston, 1986).

Pool, K. H. et al. 1994. *Waste Tank Organic Safety Project. Analysis of Liquid Pretreatment FY 1986 Progress Report. Samples from Hanford Tank 241-C-103.* PNL-9403, Pacific Northwest Laboratory, Richland, Washington.

Rochette, E. A., Harsh, J. B., and Hill, H. H. 1993. Talanta, 40(2), pp. 147-155.

Schulz, W. W. and D. M. Strachan. 1992. *Minutes of the Tank Waste Science Panel Meeting, March 25-27, 1992.* PNL-8278, Pacific Northwest Laboratory, Richland, Washington.

Seckner, A. J. 1987. MS Thesis, John Hopkins University.

Smith, R. D. and K. J. Light-Wahl. 1993. Biol. Mass. Spectrom. 22:493501.

Smith, R. D. and Udseth, H. R. 1983. Anal. Chem., 55:2266-2272.

Smith, R. D., R. R. Ogozalek Loo, M. Busman, and H. R. Udseth. 1991. Mass Spec. Rev. 10:359-451.

Toste, A. P. et al. 1986. *Hanford Tank Safety Project. Complex Concentrate Pretreatment FY-1986 Progress Report*, PNL-7687, Richland, Washington.

Yonker, C. R., Frye, S. L., Kalkwarf, D. R., and Smith, R. D. 1986. J. Phys. Chem, 90:3022-3026.

APPENDIX A

Experimental Procedures

APPENDIX A

A.0 Experimental Procedures

A.1 Derivatization Gas Chromatography/Mass Spectrometry (GC/MS)-Determination of Chelators and Chelator Fragments

Waste Sample Extraction/Derivatization

The waste sample represented a composite of several segments of actual waste obtained by core drilling the waste in Tank 241-SY-101. This material was highly radioactive, contained a high concentration of nitrate and nitrite, and the OH- concentration was 2 M. The total organic carbon (TOC) was 1.5 to 2.1%.

Hot Cell Derivatization Procedure

Approximately 2 g of the solids from the composite sample were stirred overnight with 20 mL of doubly-distilled water. The solution was filtered, and the aqueous solution was evaporated down to dryness in Reactivials (VWR Scientific) using nitrogen blowdown techniques. This involves heating the sample while blowing a steady stream of nitrogen over the sample. Approximately 2 mL of 14% BF_3/methanol (Aldrich) was added, and the sample was then heated to 100° C for 1 h. The solution was cooled, and 1 mL of chloroform was added. The entire solution was then poured into a test tube containing 2 mL of 0.1 M KH_2PO_4 adjusted to pH 7.0. The Reactivial was rinsed with 1 mL of chloroform, and this was also added to the test tube. The test tube was vortexed, and the aqueous and chloroform layers were allowed to separate. The chloroform layer, containing the derivatized organics, was retained, and the aqueous layer was discarded. At this point, approximately 90 to 95% of the radioactivity remains with either the aqueous layer or undissolved solid material. The chloroform solution was monitored for radioactivity and then removed from the hot cell for subsequent gas chromatography(GC)/electron impact mass spectrometry(MS) analysis. The derivatized waste sample was also analyzed using positive ion chemical ionization mass spectrometry to confirm parent ion assignment.

The above procedure was all done in the hot cell facilities. The hot cell facilities are used for the preparation, e.g., sample dissolution, dilution, and solvent extraction, and occasionally, the analysis of nuclear wastes. For highly radioactive wastes, e.g., 3 to 11 R/h, the hot cell must be used. This room is composed of thick walls ($\approx$ 1.3 m) equipped with a sample entry port, viewing windows (leaded glass and oil-filled), and remote manipulators, which are operated by a highly-trained specialist. When a radioactive sample is processed in the hot cell, the procedure is both time consuming and tricky. These procedures cannot be performed by just anyone, anywhere, in any laboratory, when highly radioactive samples are involved. Special training is required. Sample turnaround is much lower when using the hot-cell facilities. Wastes with low-to-moderate specific or total radioactivity, $\leq$ 1 R/h, may be prepared and analyzed outside the hot cell in a radiation hood or glove box. The actual cutoff levels which differentiate lab bench work, glove-box work, and hot-cell work is usually based upon local practice or the judgement of the resident health physicist.

Hot Cell Extraction/Radiochemical Hood Derivatization

Approximately 5 g of waste was weighed out and stirred with 10 mL of doubly-distilled water overnight. The aqueous phase was filtered through a 0.45 μm filter. The filtrate was then passed through a cation exchange column (10 g, AG50W-X8 resin), rinsed using an additional 10 mL of water to quantitatively remove the organic material from the resin. The resulting sample volume was 20 mL. After surveying the samples for radioactivity levels, the aqueous solution containing the organics was removed from the hot cell facilities.

Aliquots (2 mL) of the sample were transferred to telfon-sealed vials, evaporated to dryness using nitrogen blow down techniques, and derivatized with 2 mL of BF_3/methanol. The sample was heated to 100°C for 1 h. The sample was then hydrolyzed with a KH_2PO_4 solution and extracted with chloroform as described previously. The chloroform extract was then analyzed by Gas Chromatograph/Mass Spectrometry (GC/MS).

In calculating the concentration of organic constituents, mechanical extraction loss experienced from the initial 10 mL extraction was estimated by determining the water present in the original samples, adding the 10 mL of water used for the extraction to that water, and then subtracting the volume of water recovered to determine the mechanical loss. Water content of samples was determined by measuring the percent solids. (Appendix D)

Aliquots were also measured for LC analysis. Dilutions of the original solutions were usually necessary due to the concentration levels.

Methylation using the reaction with diazomethane, silylation by bis(trimethylsilyl)trifluoroacetamide (BSTFA), butyl esterification with butanol/HCl, chloroethyl esterification with chloroethanol/HC1, and methylation with BF_3/methanol were carried out on chelator standards obtained from Aldrich and independent sources. All mass sprectral analyses were performed on a Hewlett Packard HP 5988A GC/MS system.

Other experimental conditions are described below:

BF_3/methanol Methylation

Reaction of BF_3/Methanol with chelator standards

Approximately 1 mL of a 10% w/v solution of boron trifluoride (BF_3)/methanol (Aldrich) was added to about 5 mg of the chelator in a reaction vial, and the mixture was vortexed and heated for varying lengths of time (1 to 5 h) at 100°C, depending on the chelator being derivatized. One mL of chloroform was added to the cooled reaction mixture and vortexed. A buffer solution consisting of 1 M KH_2PO_4 was made, and the pH was adjusted to 6.92 using sodium hydroxide. When this buffer solution was added to the contents of the vial, the solution separated into two layers and an aliquot was pipetted from the bottom layer, the chloroform layer, for GC/MS analysis. Parent ion assignment was confirmed by using positive ion chemical ionization mass spectrometry.

Instrumentation

GC/MS Conditions

The instrument was equipped with a HP 5980 GC operated in the splitless mode. A fused silica column (DB-5, 30m X 0.25 mm i.d., 0.25 μm film thickness, J & W Scientific) was used. The oven temperature was typically programmed in the following manner: 50°C for 1 min, 8°C/min to 300°C, and hold at 300°C for 5 min. The mass spectrometer was tuned daily with perfluorotributylamine (PFTBA). In these studies, the mass spectrometer was scanned from 50 to 500 amu and operated in the electron impact mode (70 eV). The source temperature was 200°C, the injector port temperature was 250°C, and the interfaces were also at 250°C.

Chemical ionization was carried out with both methane and isobutane in both positive ion and negative ion chemical ionization modes. The temperature of the source for positive ion chemical ionization MS was 200°C and 120°C for negative ion chemical ionization. The mass spectrometer was scanned from 100 to 600 amu in the negative ion mode and 70 to 500 in the positive ion mode.

Accurate Mass Measurements

Accurate mass measurements were performed on a VG 70-EHF double-focusing mass spectrometer equipped with a VG 11-250 data system. The instrument was tuned to a resolution of 5000 (10% valley definition). Data were acquired by scanning the magnetic field exponentially down over the mass range of 230 to 90 at a rate of 3 sec per mass decade. Instrument tuning and real-time mass measurements were performed by leaking perfluorokerosene into the electron impact ion source from the septum inlet reservoir. Computer-assisted accurate mass assignments and subsequent elemental compositions were made on data obtained from averaging four consecutive scans over the gas chromatographic elution profile of the analyte. The instrument was equipped with a Varian Model 3700 gas chromatograph. The GC was fitted with 30 m X 0.25 mm i.d. DB-5 capillary column (J & W Scientific, Folsom, California). The GC oven temperature was held at 50°C for 2 min, then programmed at 5°C/min to 250°C.

A.2 Analysis of Acid and Base-Neutral Solvent Extracts

Sample Preparation

A 2-g aliquot of a composite sample (pH 13) was mixed with 10 mL of methylene chloride and vortexed for three min. The solution was filtered and concentrated to approximately 100 μL for GC/MS analysis. The pH of the original solution was then adjusted to 3 with the addition of HCl. The slurry was then mixed with 10 mL of methylene chloride and vortexed for 3 min. The solution was then filtered and concentrated to approximately 100 μL for analysis using GC/MS.

Instrumentation

The extracts were analyzed using a JEOL SX 102/SX 102 double focusing tandem mass spectrometer in the electron impact mode and equipped with a JEOL UNIX data system. Instrument tuning and real-time mass measurements were performed by leaking perfluorokerosene (PFK) into the electron impact ion source from the septum inlet reservoir. The instrument was equipped with a Hewlett-Packard 5890 gas chromatograph. The GC was fitted with a 30 m X 0.25 mm i.d. DB-5 capillary column (J & W

Scientific, Folsom, California). The GC oven temperature was held at 50°C for 1 min, then programmed at 8°C/min to 300°C.

A.3 High Resolution Mass Spectrometry-Accurate Mass Determination, Empirical Formula

Accurate mass measurements were performed on a JEOL SX 102/SX 102 double focusing tandem mass spectrometer equipped with a JEOL UNIX data system. The instrument was tuned to a resolution of 10,000 (10% valley definition). Data was acquired by scanning the magnetic field exponentially down over the mass range of 30 to 600 at a rate of second per mass decade. Instrument tuning and real-time mass measurements were performed by leaking PFK into the electron impact ion source from the septum inlet reservoir. Computer-assisted accurate mass assignments and subsequent elemental compositions were made on data obtained from averaging four consecutive scans over the gas chromatographic elution profile of the analyte. The instrument was equipped with a Hewlett-Packard 5890 gas chromatograph. The GC was fitted with a 30 m X 0.25 mm i.d. DB-5 capillary column. The GC oven temperature was held at 50°C for 2 min, then programmed at 5°C/min to 250°C.

A.4 Thermospray LC/MS of Low Molecular Weight Acids

Reagents

Gluconic acid, sulfuric, formic, acetic, phosphoric, and hydrochloric acid were obtained from Aldrich. Gluconic acid was in the form of the potassium salt. Formic acid and acetic acid were diluted from the concentrated acid reagents. Tartaric acid and hexanoic acid were obtained from Chem Services. The sulfuric acid, acetic acid, phosphoric acid, and hydrochloric acid used in preparing the mobile phases were diluted from the concentrated acid reagents. Milli-Q water was used for all dilutions. N-Nitroso-iminodiacetic acid was synthesized in the following manner.

Synthesis of N-Nitroso-iminodiacetic acid (NIDA)

The synthetic procedure was similar to that reported in the literature (Warren and Malec 1972). To a 500-mL, four-necked flask—equipped with an overhead stirrer, an addition funnel, and a thermometer—were added 26.6 g (20 mmoles) of iminodiacetic acid (Aldrich) and 200 mL of 1 M phosphoric acid. The contents of the flask were heated to 50°C, and a solution of 27.6 g (400 mmoles) of sodium nitrite in 60 mL of water was added dropwise. The reaction was then stirred for 1 min and extracted with 5 100-mL portions of diethyl ether. The ethereal extract was dried ($MgSO_4$) and concentrated to yield a yellowish white residue, which after recrystallization from ethyl acetate-hexane afforded 13 g of nitroso acid.

Instrument Conditions

Liquid Chromatography

A Bio-rad HPLC Organic Acids column, Aminex Ion Exclusion, HPX-87H, 300 X 7.8 mm, with compatible guard column was used. The mobile phase for this part of the work was 0.001 N HCl (isocratic). The LC oven temperature was 40°C, and the flow rate was 0.6 mL/min. A typical run time was 25 min. Standards of organic acids were analyzed using direct flow injection and after introduction onto the analytical column. A mixture of organic acids was also analyzed after separation by the analytical column.

Mass Spectrometry

The thermospray analyses were performed using the HP 5988A LC/MS in the isocratic mode. The ion source was 275°C, and the stem initial temperature was 100°C. Typical values for the tip and the vapor were 230°C and 272°C, respectively. Filament operation was in both the on-and-off modes. The multiplier voltage was 2692 V, and the scan range was either 79 to 500 or 92 to 300 amu, depending on the mixtures being analyzed. The injection volume was either 10 μL or 20 μL, depending on the concentration of the sample.

The instrument was tuned with polyethylene glycol (PEG) tuning solution to give maximum abundance of ions. It should be noted that the thermospray ion source should be cleaned approximately once a week to remove nonvolatile chloride salts resulting from the use of HCl as the mobile phase. Also, since HCl possesses corrosive effects on metal surfaces, water was flushed through both the HPLC and thermospray system at the end of the day. As long as these cleaning and flushing procedures were followed, no detrimental effects of the thermospray or chromatographic equipment were observed.

Actual Waste Sample

The waste sample represented a composite of several segments of actual waste obtained by core drilling the waste in Tank 101-SY. This material was highly radioactive, contained a high concentration of nitrate and nitrite, and the OH- concentration was 2 M. The TOC was 1.5 to 2.1%.

The actual waste sample was passed through a Bio-Rad analytical grade cation exchange column (AG 50W-X8, 50-100 mesh, hydrogen form) in a remote handling hot cell which removed almost all of the radioactivity due to primary fission products in the waste (sometimes down nearly background levels) before being brought to the instruments for analysis. The hot-cell facilities are used for the preparation, e.g., sample dissolution, dilution, and solvent extraction, and occasionally, the analysis of nuclear wastes. For highly radioactive wastes, e.g. 3 to 11 R/h, the hot cell must be used. This room is composed of thick walls ($\approx$ 1.3 m) equipped with a sample entry port, viewing windows (leaded glass and oil-filled), and remote manipulators, which are operated by a highly-trained specialist. When a radioactive sample is processed in the hot cell, the procedure is both time consuming and difficult. These procedures can not be performed by just anyone, anywhere, in any laboratory, when highly radioactive samples are involved. Special training is required. Sample turnaround is much lower when using the hot cell facilities. Wastes with low-to-moderate specific or total radioactivity, $\leq$ 1R/h, may be prepared and analyzed outside the hot cell in a radiation hood or

glove box. The actual cutoff levels that differentiate lab bench work, glove-box work, and hot-cell work is usually site specific, based upon local practice or the judgment of the resident health physicist.

A 1-g aliquot of the waste sample was weighed and placed in a 25.0 mL volumetric flask. The sample was then neutralized with 0.001 N HCl to the pH of the mobile phase using an Orion extended scale pH meter. The solution was then diluted to volume using Milli-Q water. An aliquot of the solution was filtered into an LC vial using a Gelman Acrodisc LC13, 0.45 μm syringe-tip filter. Approximately 20 μL was used for HPLC or thermospray LC/MS analysis.

A.5 ELectrospray MS

Electrospray ionization MS data of the chelators was obtained on the JEOL SX102/SX102 mass spectrometer fitted with an ESI source. This technique is being applied to the analysis of chelators as shown in Figures 3.12 to 3.18. The instrumental conditions were as follows: magnetic field scanned from 0-2000 Daltons, 30 ms cycle time, data accumulated for approximately three minutes, negative ion mode detection. The sample solutions were made by dissolving stock chelators in 25%/75% isopropanol/water with a final chelator concentration of 1mM, unless otherwise noted. The solutions were continuously infused to the ESI source at 1-2 μL/min. A counterflow of heated N_2 was used to aid in desolvation.

A.6 FT Raman

The Raman spectrum can yield organic and inorganic functional group information on a sample in much the same way as infrared spectroscopy does. An advantage of Raman over infrared spectroscopy is that there is no need to put the sample into an infrared transparent matrix. For instance, Raman spectra can be taken directly on samples that are contained in glass vials. Because functional group analysis may be required as part of the remediation efforts at the Hanford Nuclear Site, several examples of typical waste tank contents were characterized by FourierTransform Raman spectroscopy (FT-Raman). These samples included EDTA, HEDTA, IDA,NIDA, citric acid, lauric acid and sodium nitrite.

The samples were characterized by FT-Raman using two sampling methods. In the first sampling method, several crystals of each substance were placed on a gold coated microscope slide and characterized directly using the FT-Raman microscope (microprobe). The microprobe permits samples as small as a few microns to be characterized. In this instance, a single crystal that was about 50 μm across was characterized. Each sample crystal was illuminated with approximately one watt of laser power. A liquid nitrogen cooled germanium detector was used, which is typical for microprobe work. The spectra were taken at 8 cm-1 resolution and are the result of 1000 co-added scans, which takes about 20 minutes. The spectra were triangularly apodized and had two orders of zero-filling before the Fourier transformation. As can be seen, excellent spectra were obtained for the materials.

The other method used a fiber optic interface that is designed to characterize samples while still in their bottles. In this instance a room temperature indium-gallium-arsenide (InGaAs) detector was used. In these instances 100 scans were coadded. These spectra were also taken at 8 cm-1 resolution

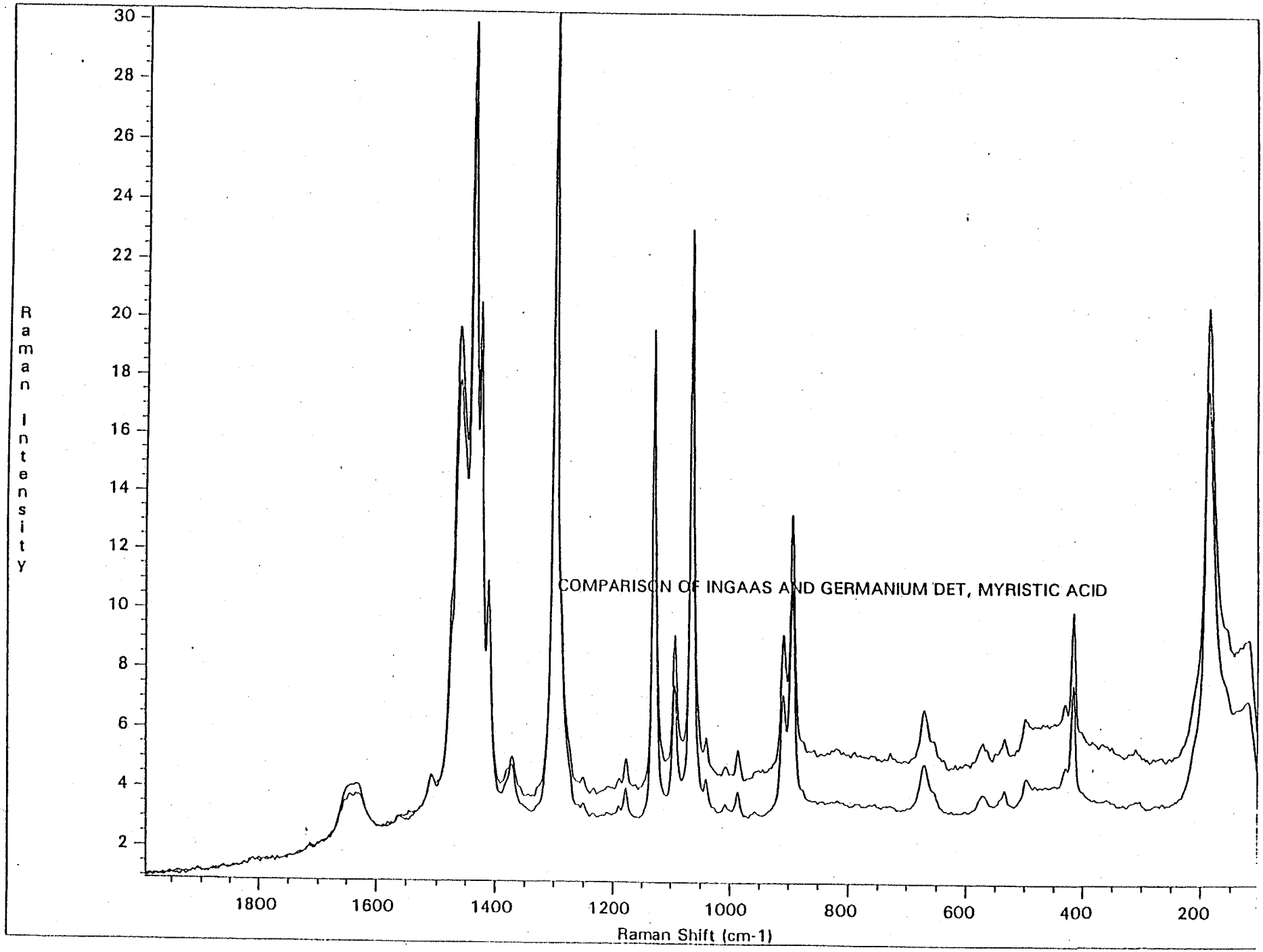
and were triangularly apodized and had two orders of zero-filling before apodization. Here again, excellent spectra were obtained, although using the InGaAs reduces the signal-to-noise ratio somewhat.

A.7 SFE

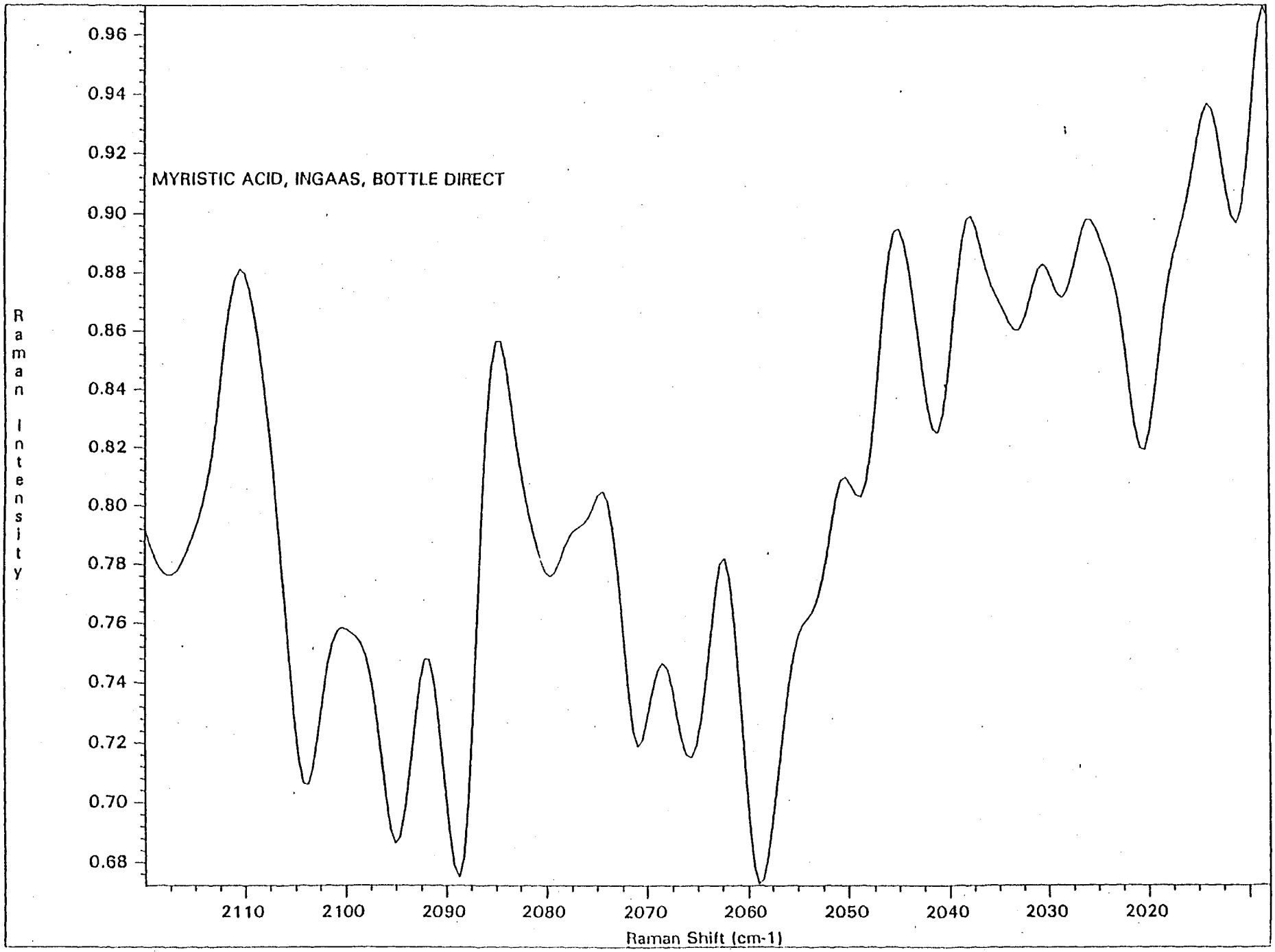
Preliminary work in our laboratory has identified a possible method which will allow the full benefits of SFE to be applied to the extraction of organic acids from mixed wastes as a prelude to characterization. Several authors have demonstrated the use of in situ SFE derivatization to make highly polar compounds more amendable to SFE extraction. To check the viability of this approach a model system was extracted using in situ SFE derivatization. EDTA and lauric acid were added to sand and then derivatized. Derivation was performed by a several step procedure. First the common alkylation reagent boron trifluoride in methanol (BF3/MeOH) was added directly to the sample once it was in the extraction thimble. Supercritical carbon dioxide modified with methanol was then pumped into the extraction thimble. This was then allowed to remain in a static state at a temperature of 100° C for a period of one hour. At the end of this time the derivatized EDTA was removed from the sand by using supercritical fluid carbon dioxide modified with 10%methanol. The derivatized acids were trapped on stainless steel bearings after extraction. These were removed from the trap by using approximately 1 ml of hexane. A small aliquot of this hexane was then injected into the gas chromatography/mass spectrometer. It was found that these compounds were successfully derivatized and extracted from the sand. It was also expected that any radioactive isotopes would remain in the matrix being extracted; that is, the extracted organic acids would of been free of radiological activity.

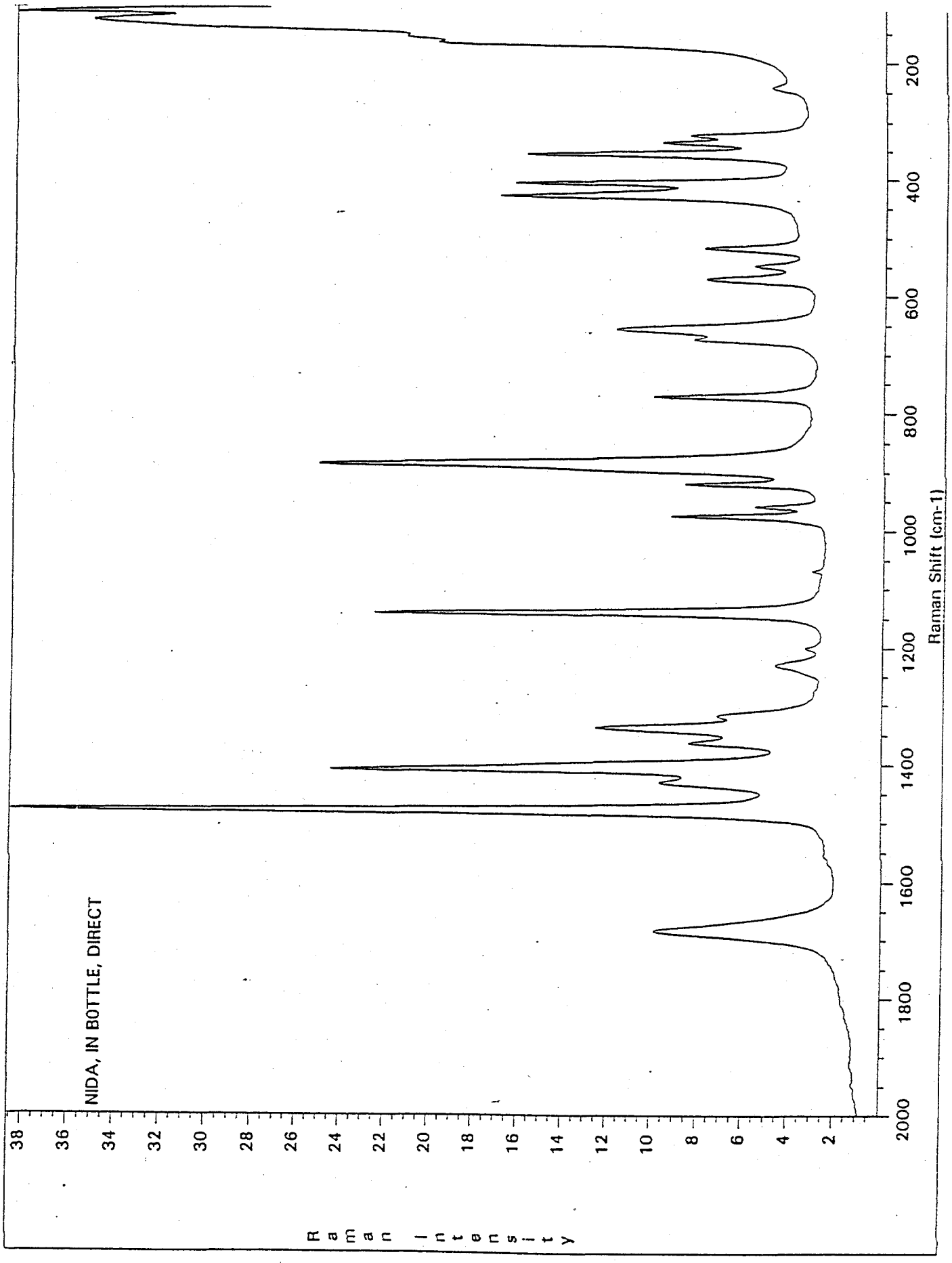
APPENDIX B

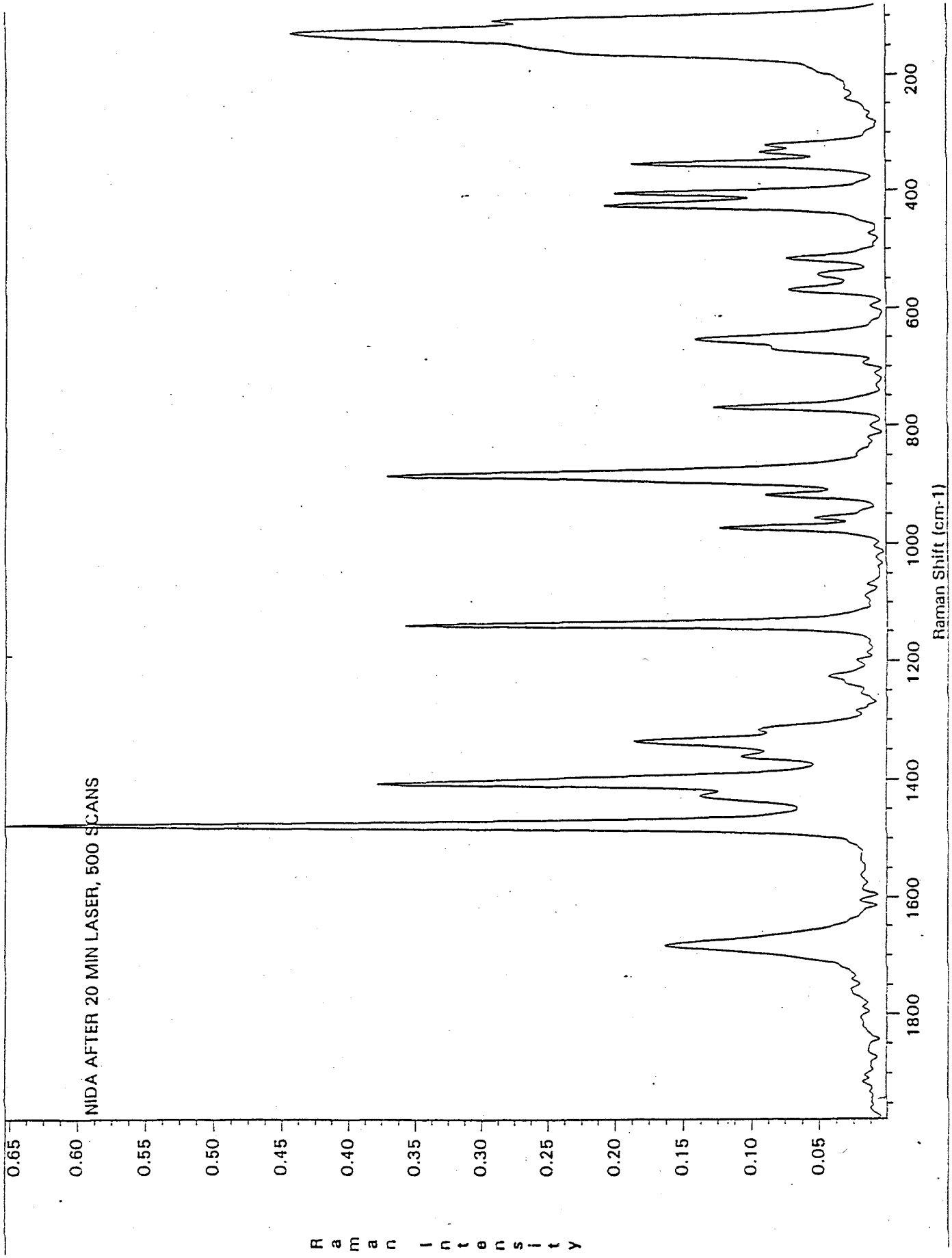
Additional Raman Spectra

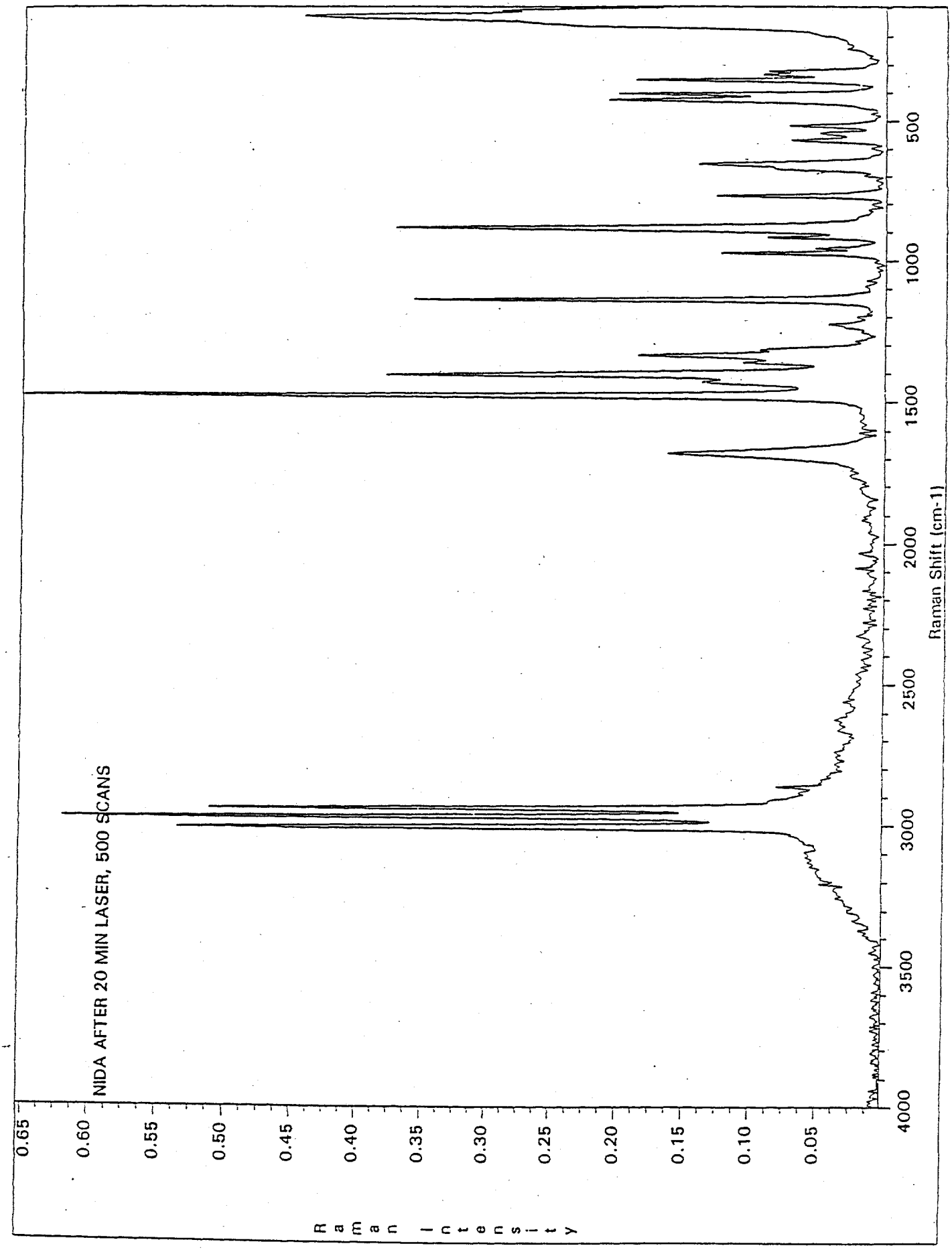

COMPARISON OF INGAAS AND GERMANIUM DET, MYRISTIC ACID
Raman Intensity
Raman Shift (cm-1)
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
1800
1600
1400
1200
1000
800
600
400
200

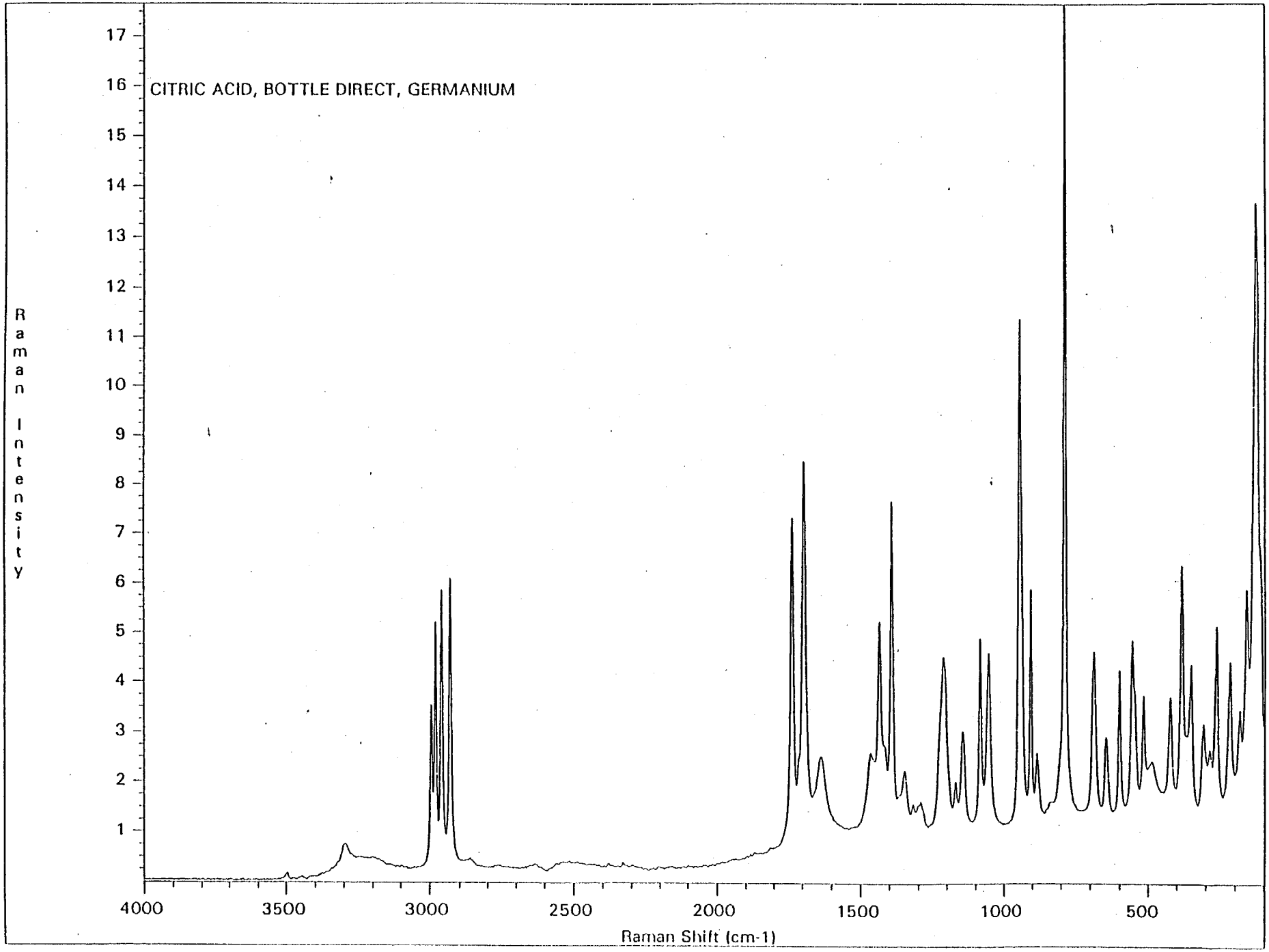
B.1

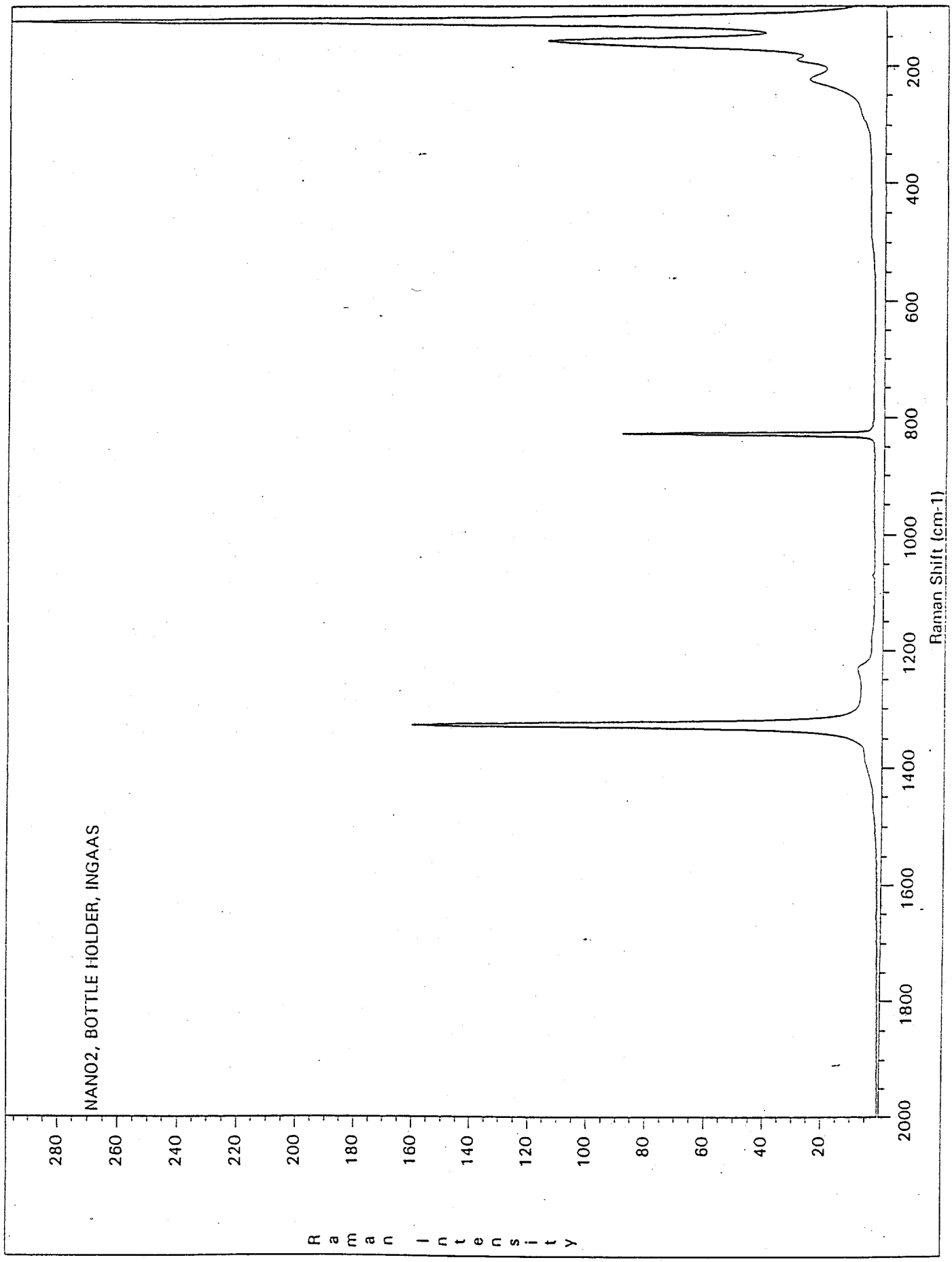

MYRISTIC ACID, INGAAS, BOTTLE DIRECT
Raman Intensity
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82
0.80
0.78
0.76
0.74
0.72
0.70
0.68
2110
2100
2090
2080
2070
2060
2050
2040
2030
2020
Raman Shift (cm-1)


NIDA, IN BOTTLE, DIRECT
Raman Intensity
Raman Shift (cm-1)
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
2000
1800
1600
1400
1200
1000
800
600
400
200


NIDA AFTER 20 MIN LASER, 500 SCANS
Raman intensity
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
1800
1600
1400
1200
1000
800
600
400
200
Raman Shift (cm-1)


NIDA AFTER 20 MIN LASER, 500 SCANS
Raman Intensity
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
4000
3500
3000
2500
2000
1500
1000
500
Raman Shift (cm-1)


CITRIC ACID, BOTTLE DIRECT, GERMANIUM
Raman Intensity
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
4000
3500
3000
2500
2000
1500
1000
500
Raman Shift (cm-1)


NANO2, BOTTLE HOLDER, INGAAS
Raman Intensity
Raman Shift (cm-1)
280
260
240
220
200
180
160
140
120
100
80
60
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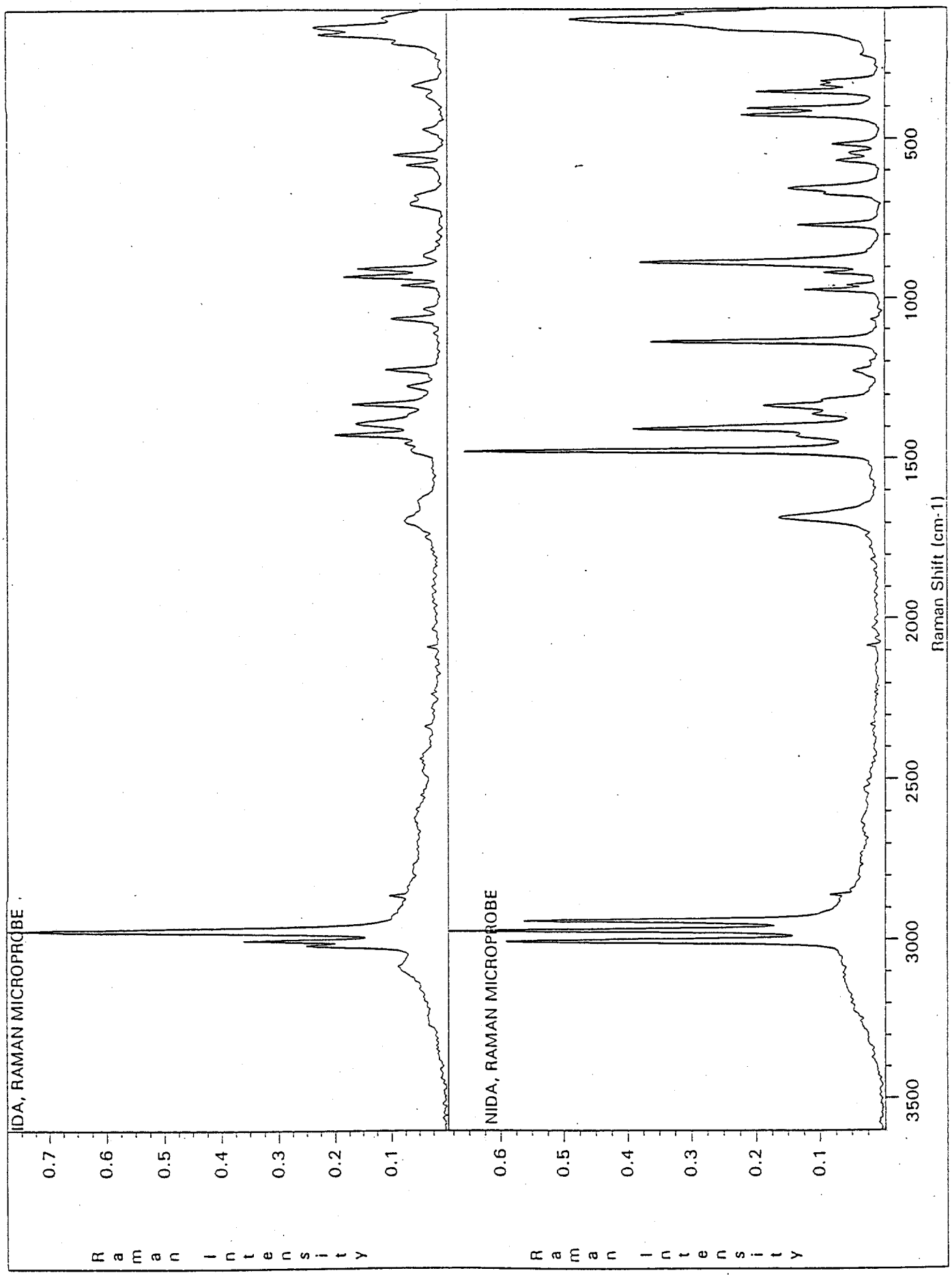
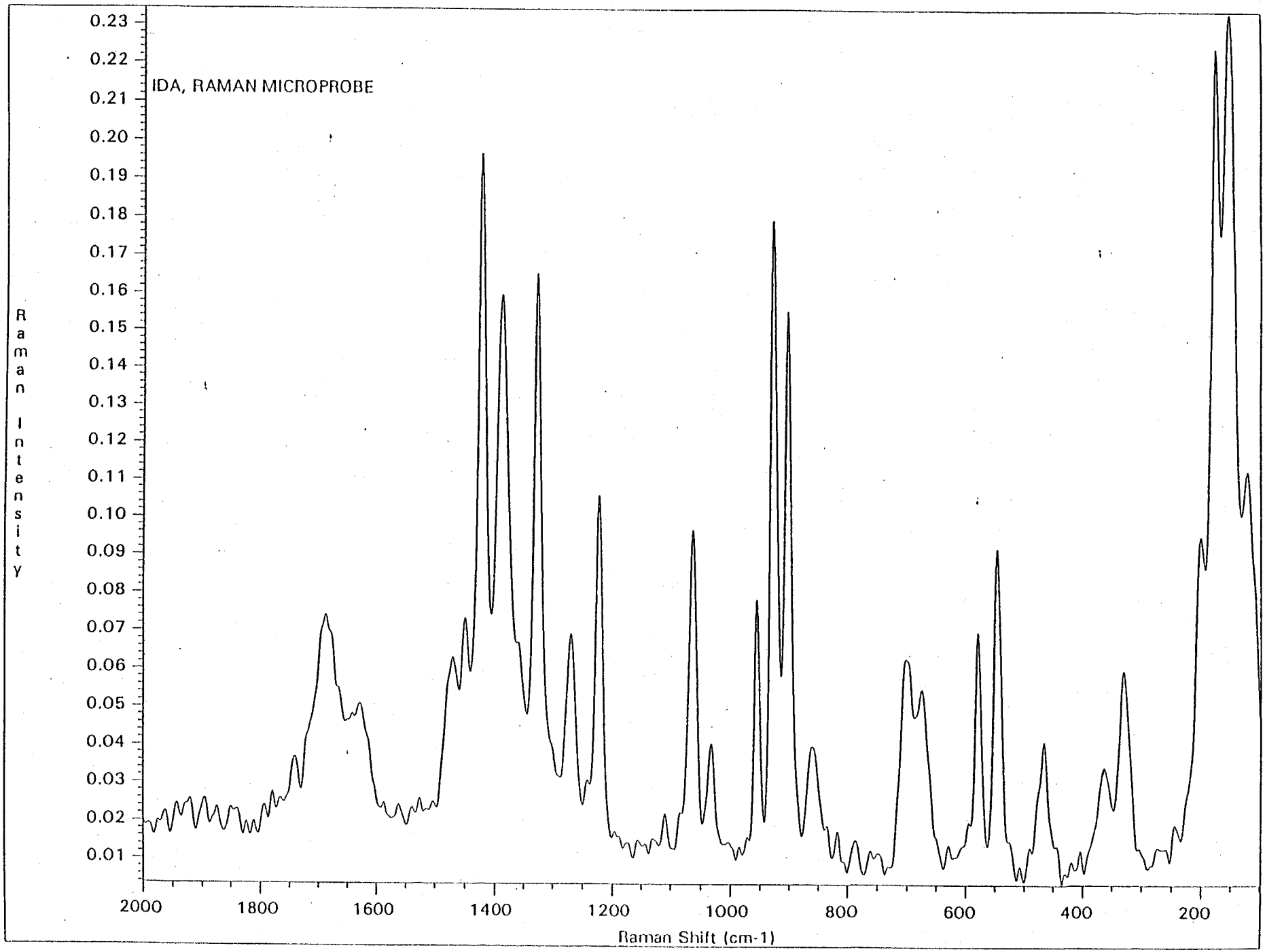
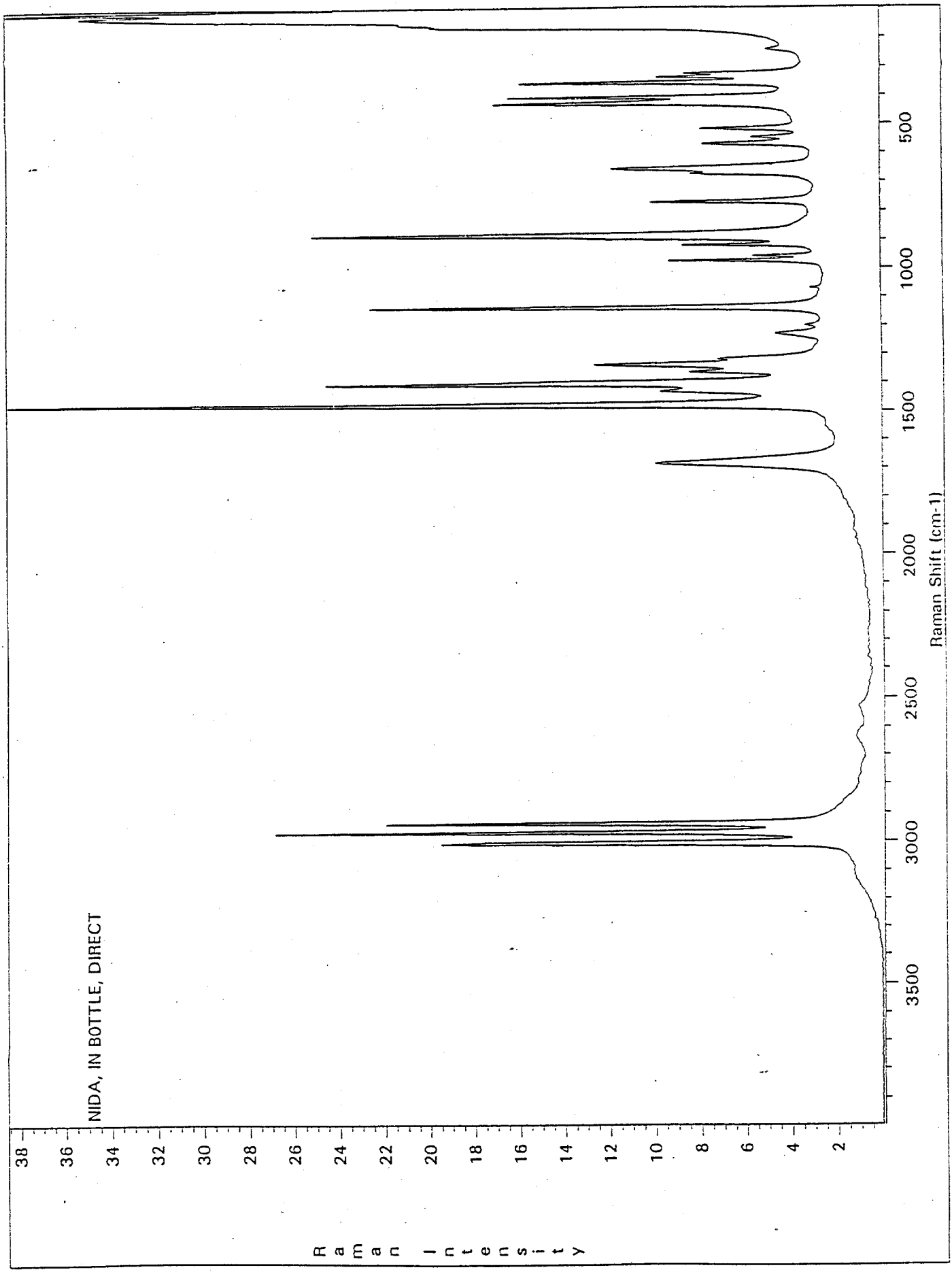
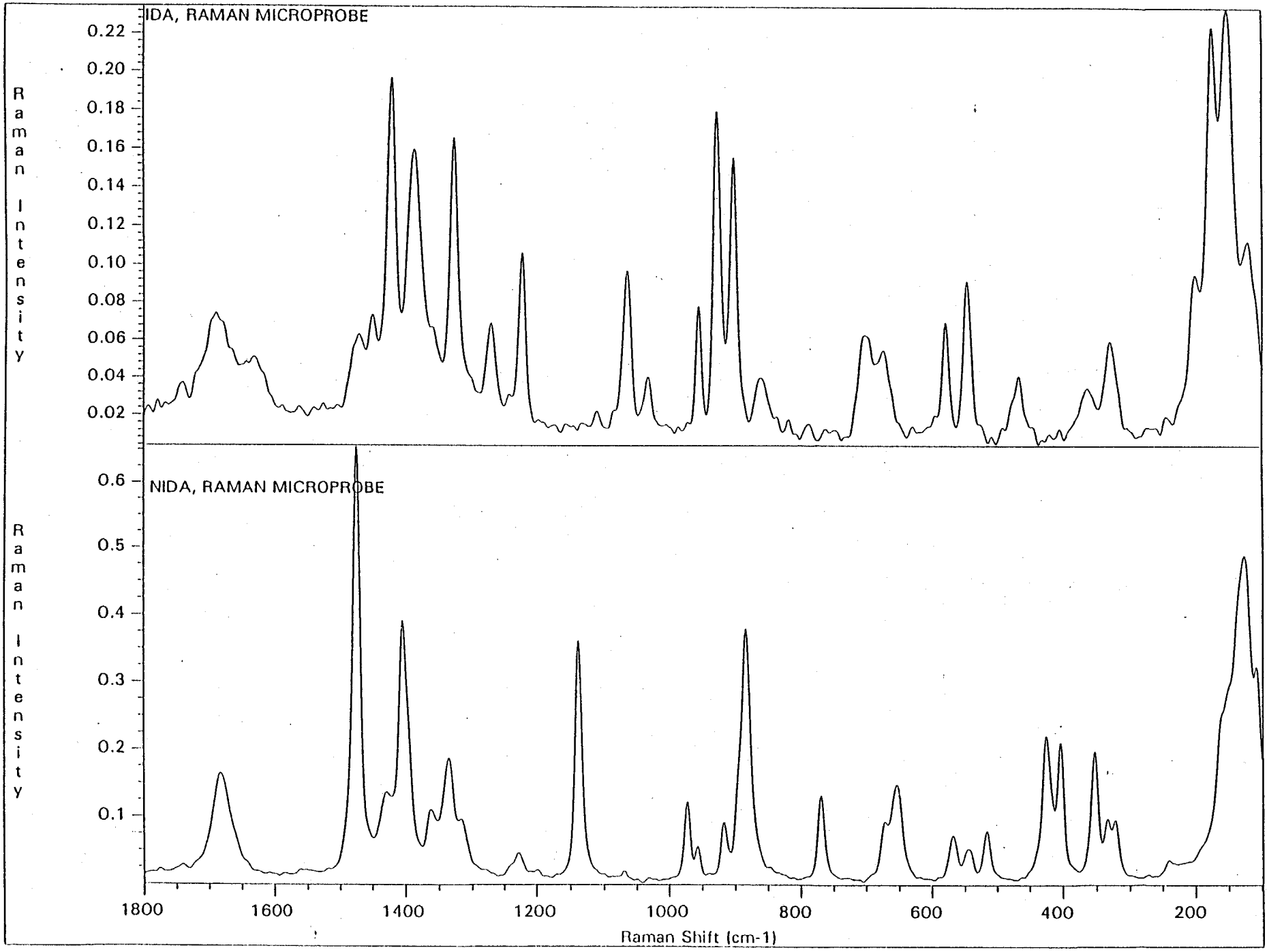
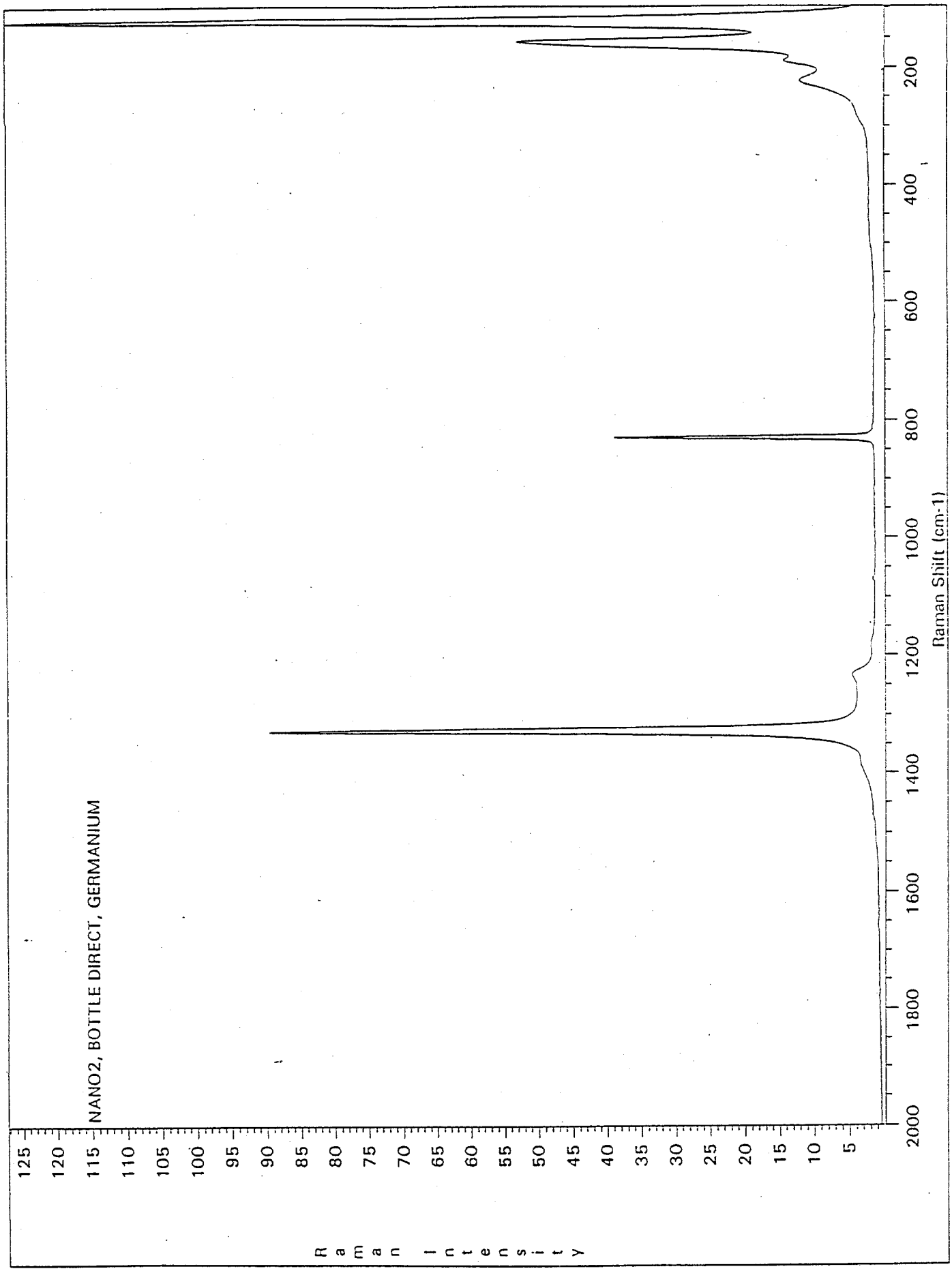
20
2000
1800
1600
1400
1200
1000
800
600
400
200

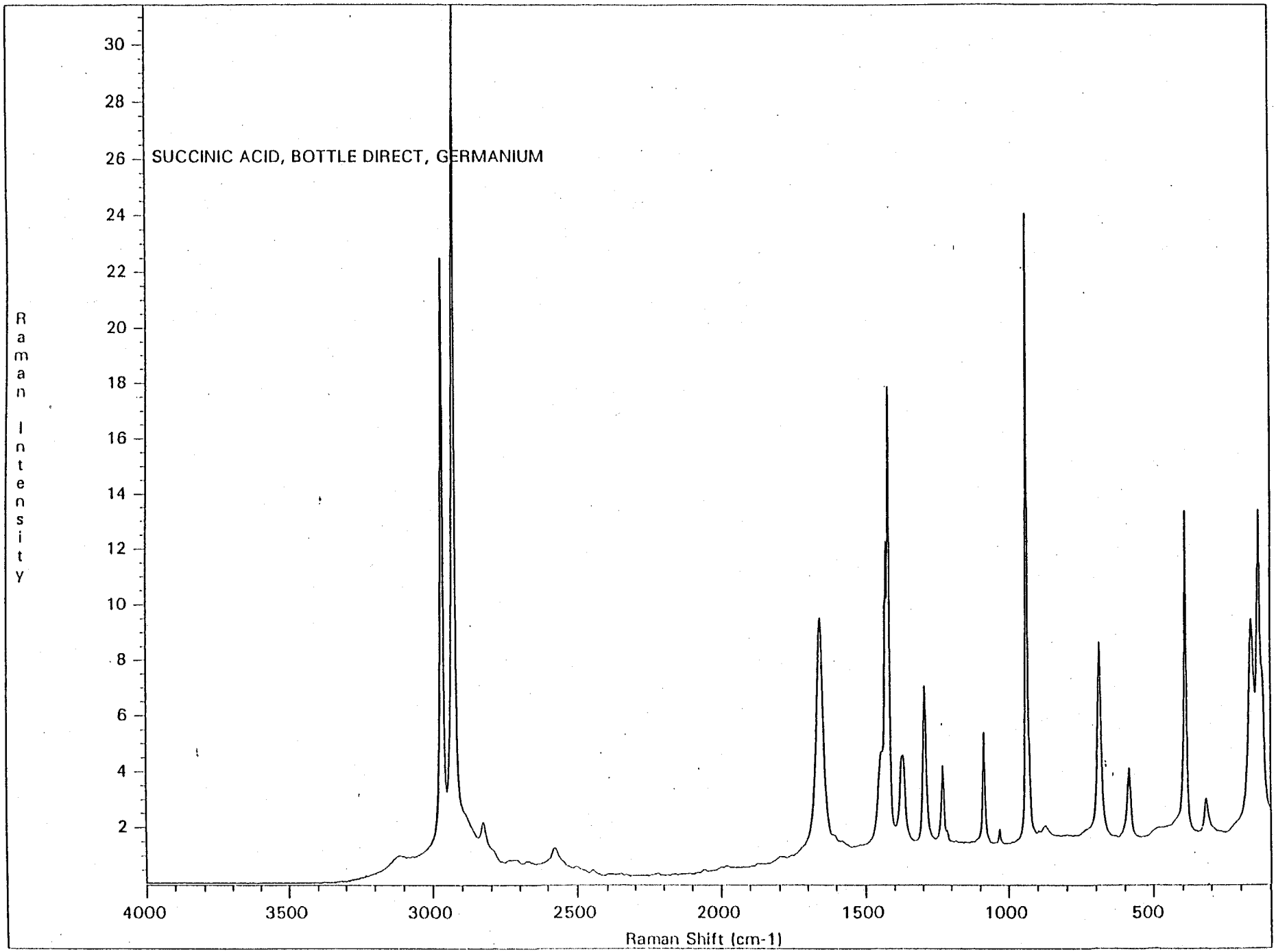

IDA, RAMAN MICROPROBE
NIDA, RAMAN MICROPROBE
Raman Intensity
Raman Shift (cm-1)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
500
1000
1500
2000
2500
3000
3500

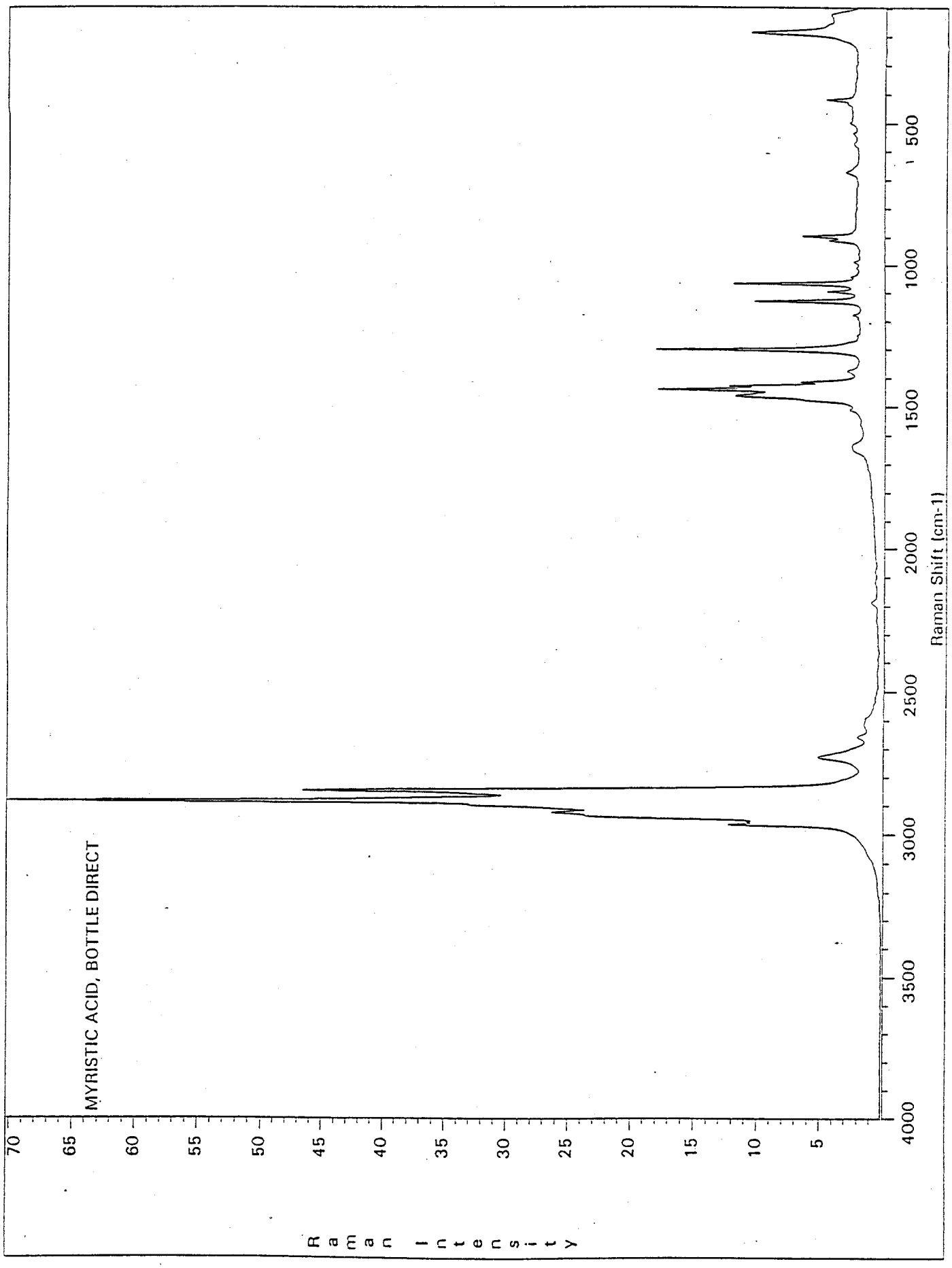

IDA, RAMAN MICROPROBE
Raman Intensity
0.23
0.22
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
2000
1800
1600
1400
1200
1000
800
600
400
200
Raman Shift (cm-1)

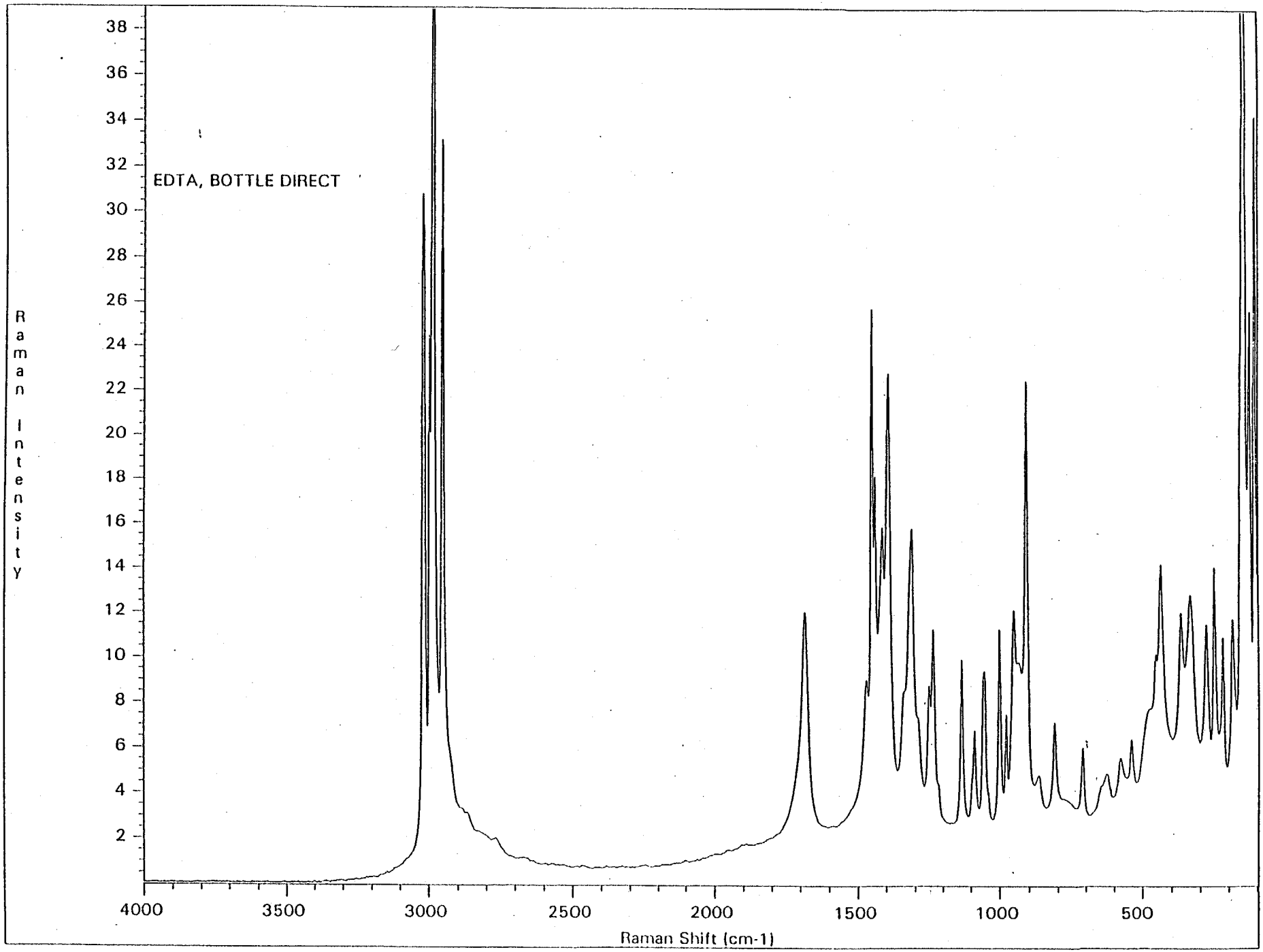

NIDA, IN BOTTLE, DIRECT
Raman Intensity
Raman Shift (cm-1)
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
3500
3000
2500
2000
1500
1000
500

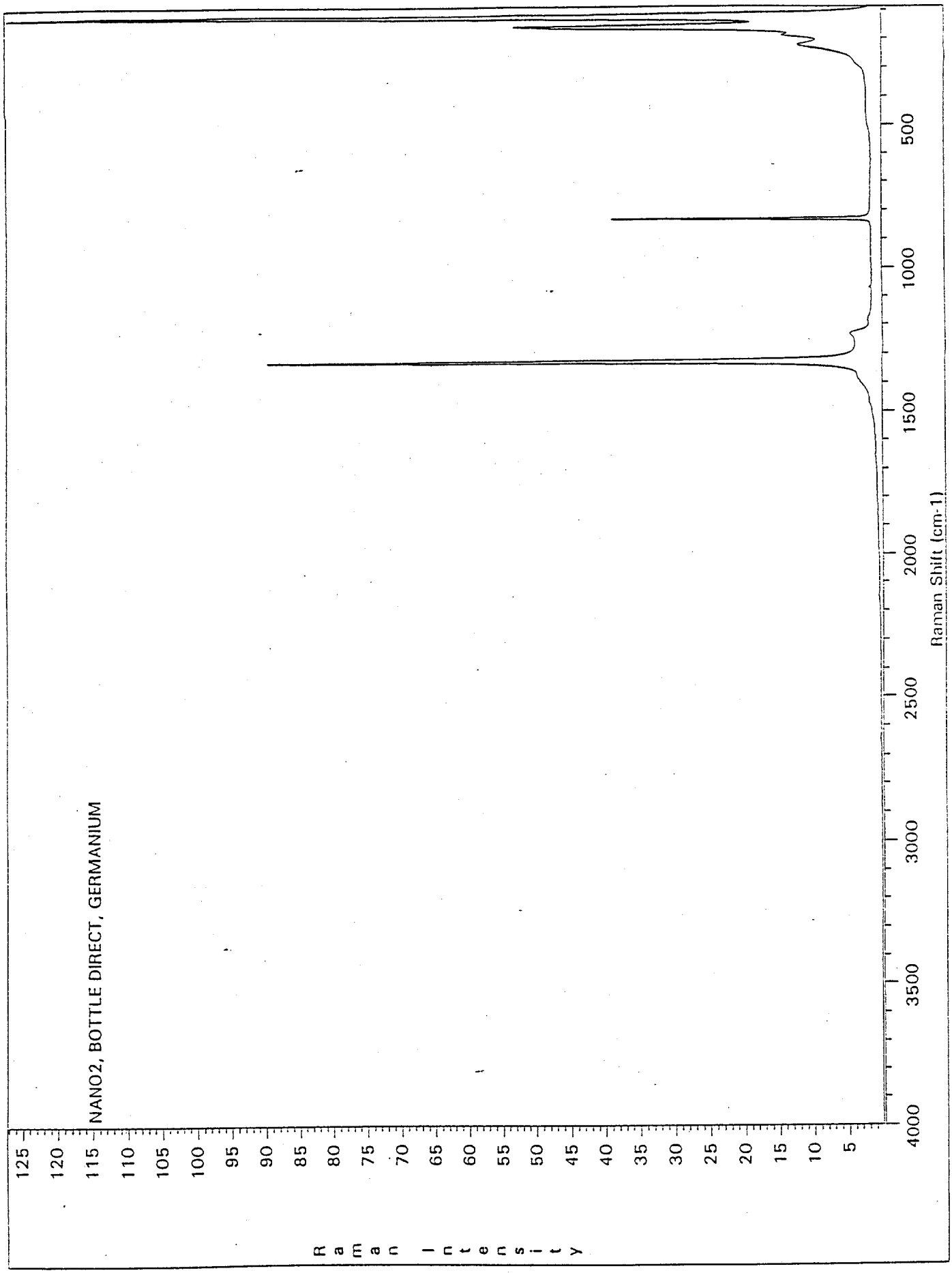

IDA, RAMAN MICROPROBE
Raman Intensity
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
NIDA, RAMAN MICROPROBE
Raman Intensity
0.6
0.5
0.4
0.3
0.2
0.1
1800
1600
1400
1200
1000
800
600
400
200
Raman Shift (cm-1)

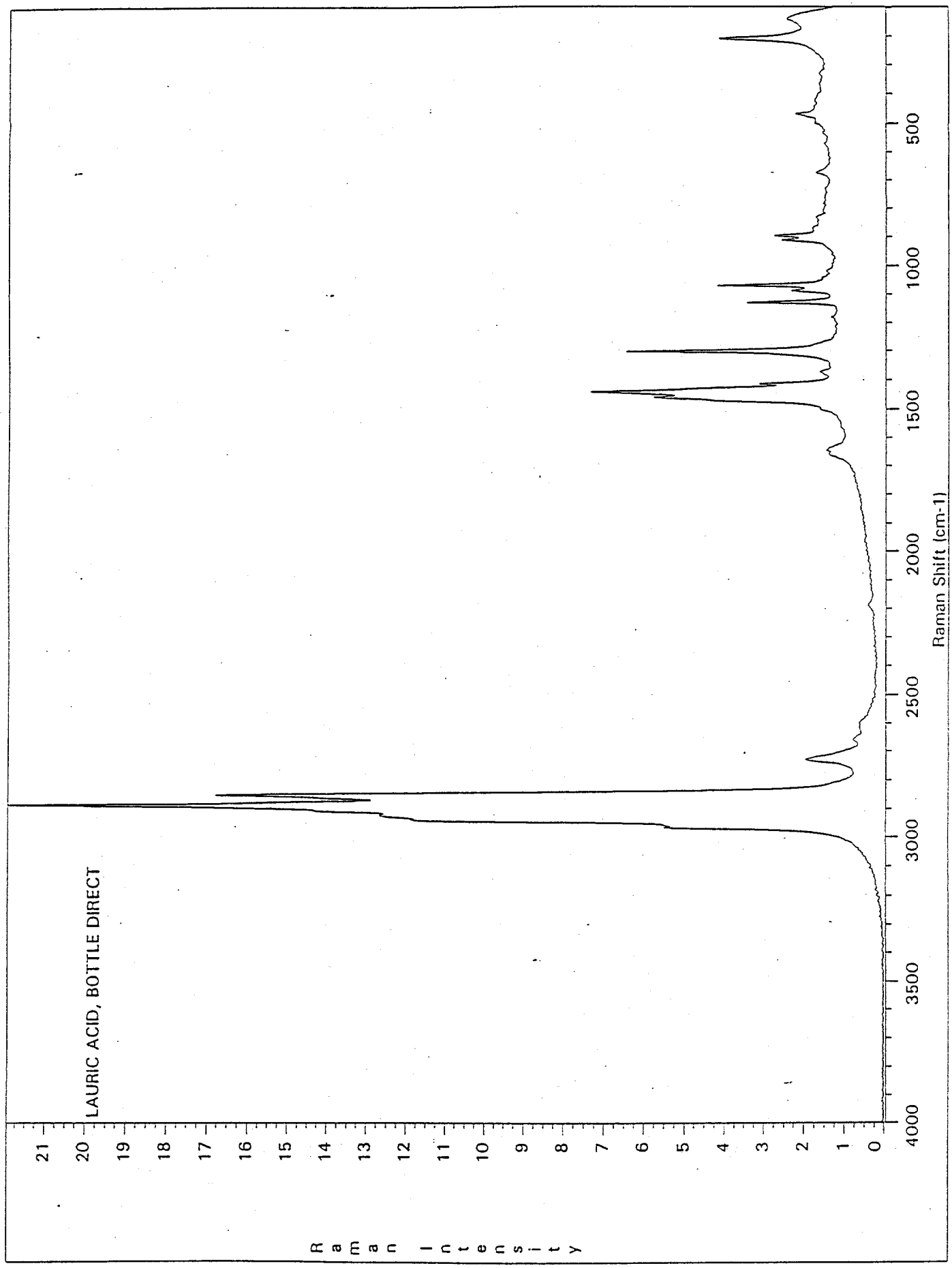

NANO2, BOTTLE DIRECT, GERMANIUM
Raman Intensity
Raman Shift (cm-1)
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
2000
1800
1600
1400
1200
1000
800
600
400
200


SUCCINIC ACID, BOTTLE DIRECT, GERMANIUM
Raman Intensity
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
4000
3500
3000
2500
2000
1500
1000
500
Raman Shift (cm-1)


MYRISTIC ACID, BOTTLE DIRECT
Raman Intensity
Raman Shift (cm-1)
70
65
60
55
50
45
40
35
30
25
20
15
10
5
4000
3500
3000
2500
2000
1500
1000
500


EDTA, BOTTLE DIRECT
Raman Intensity
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
4000
3500
3000
2500
2000
1500
1000
500
Raman Shift (cm-1)


NANO2, BOTTLE DIRECT, GERMANIUM
Raman Intensity
Raman Shift (cm-1)
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
4000
3500
3000
2500
2000
1500
1000
500


LAURIC ACID, BOTTLE DIRECT
Raman Intensity
Raman Shift (cm-1)
0
1
2
3
4
5
6
7
8
9
10
11
12
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15
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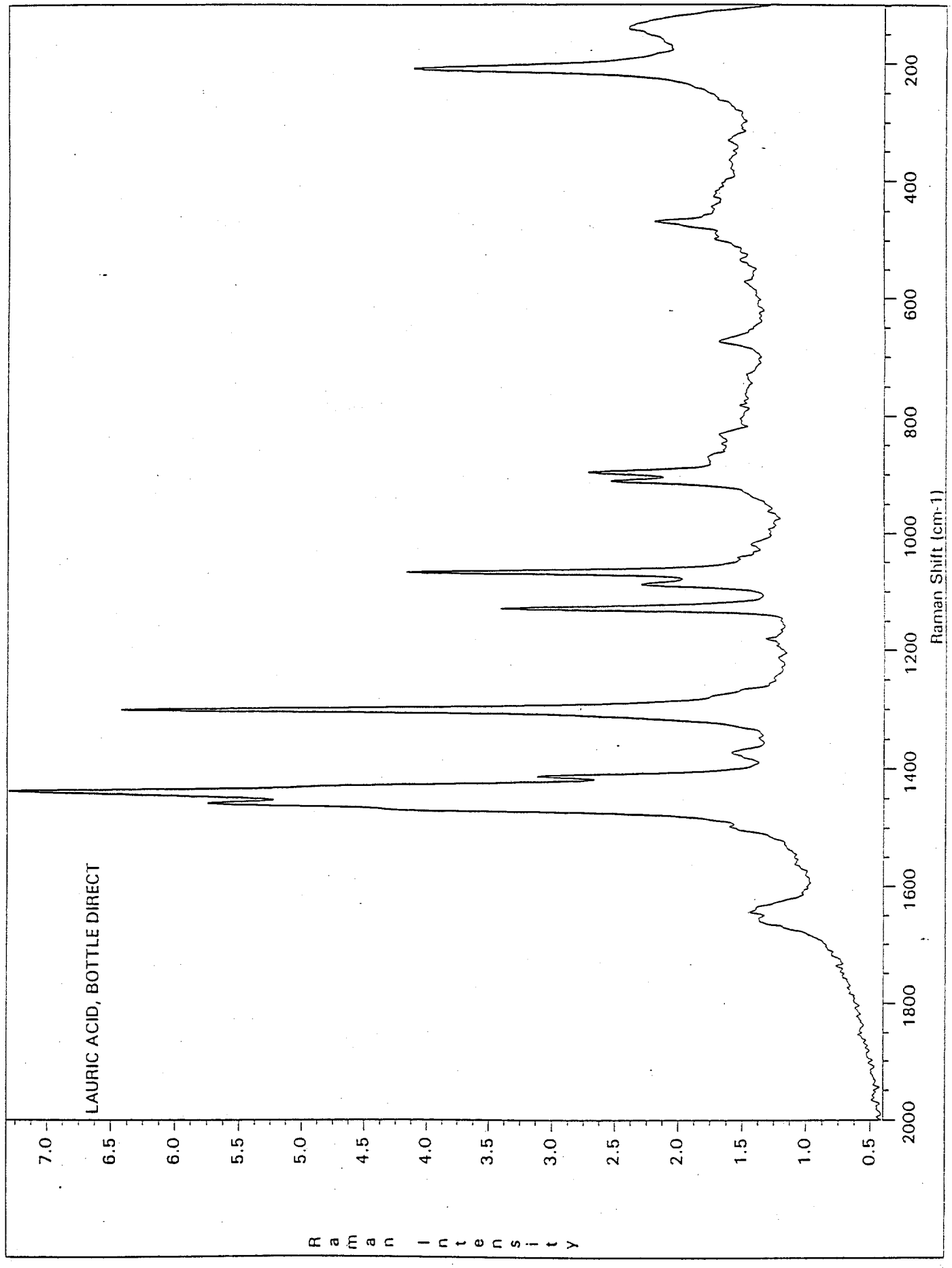
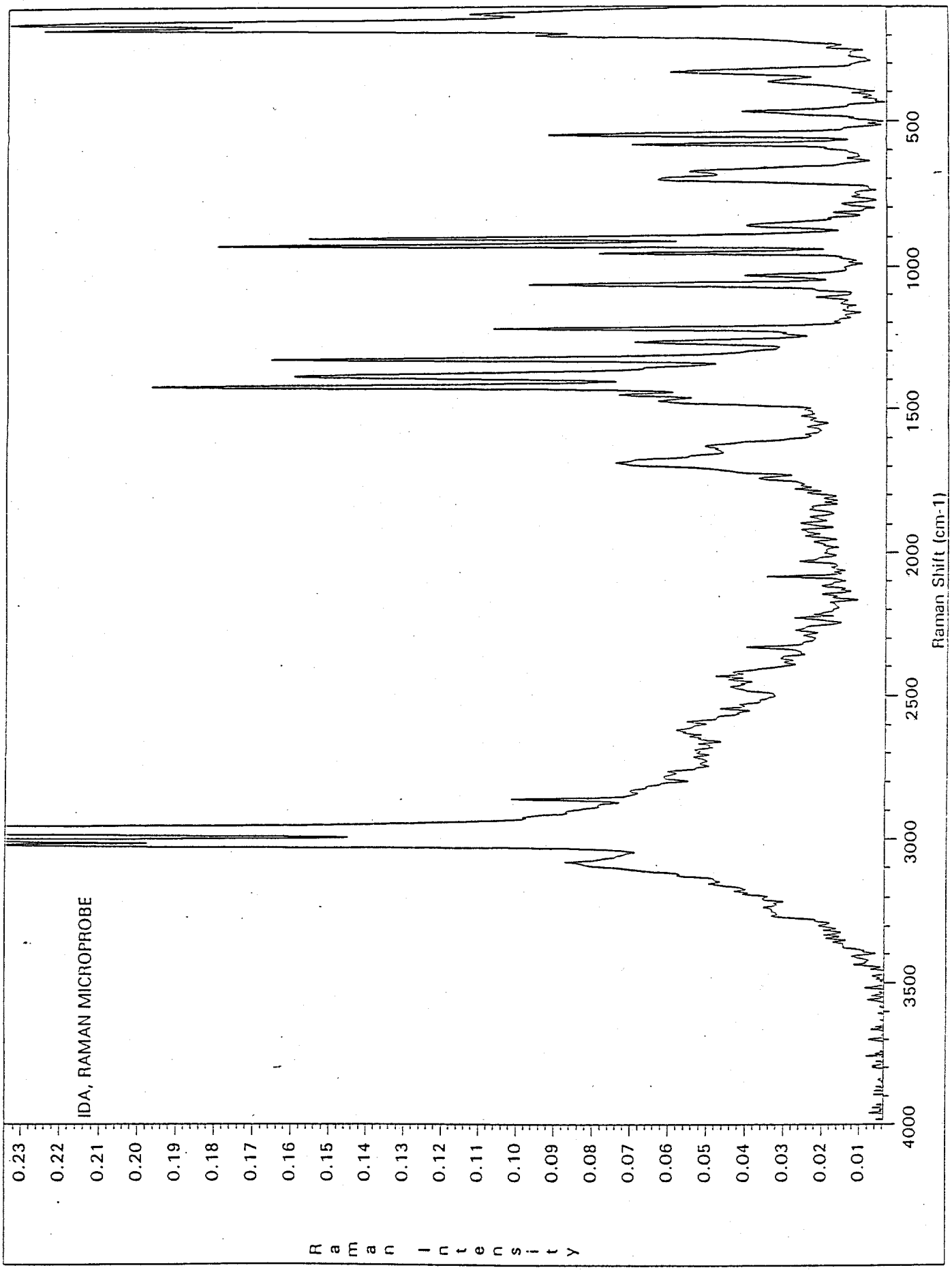
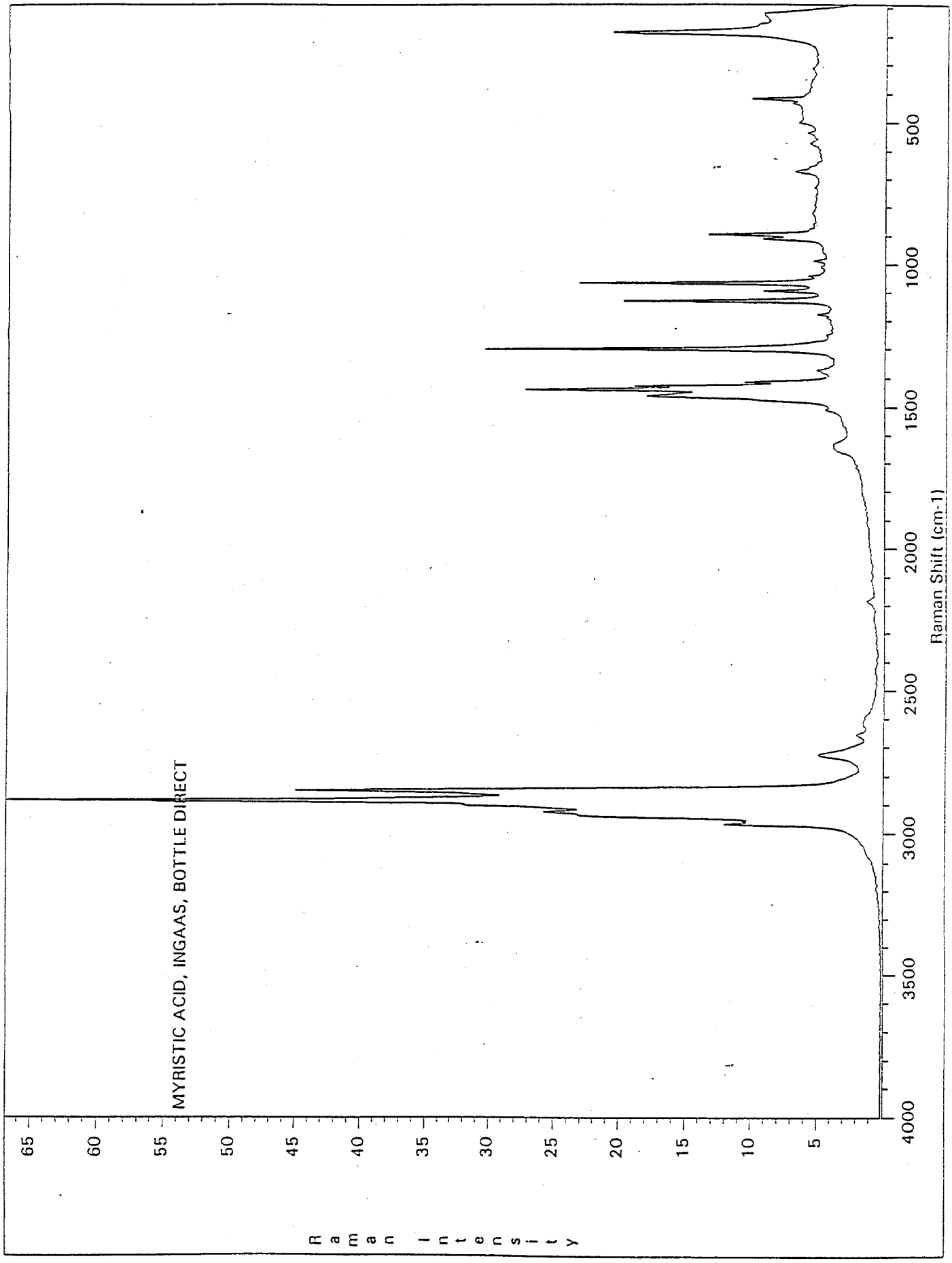
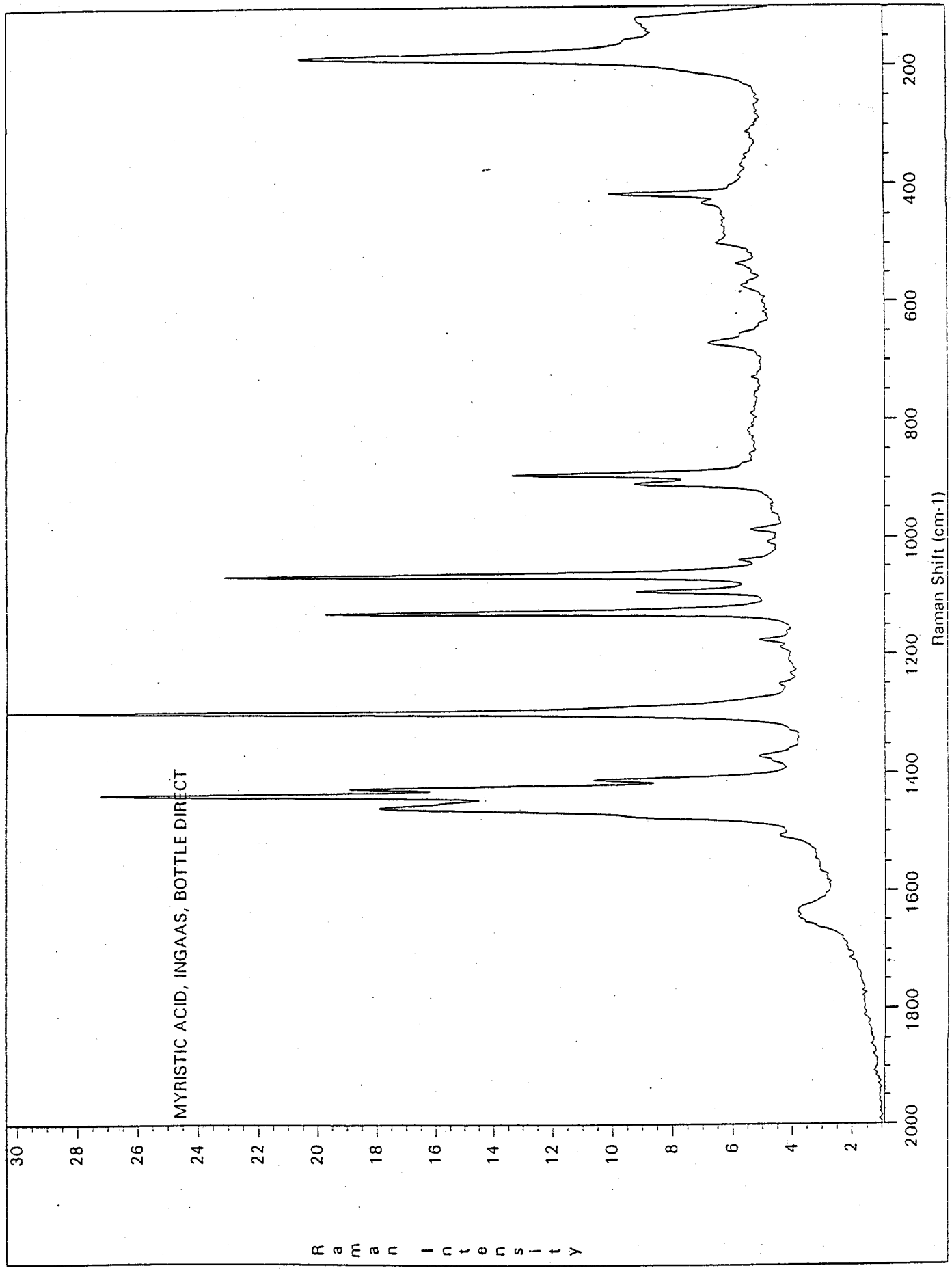
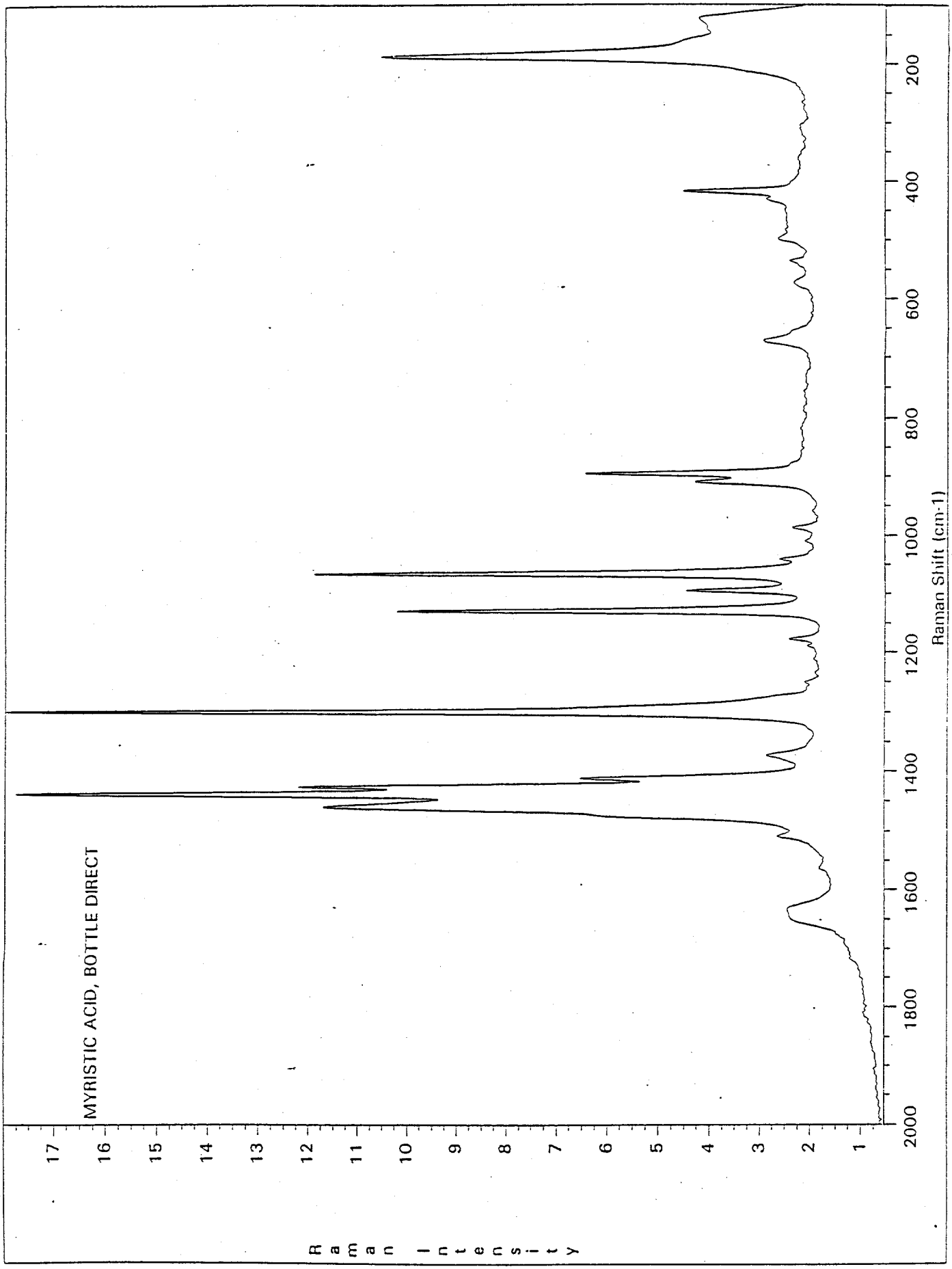
19
20
21
4000
3500
3000
2500
2000
1500
1000
500

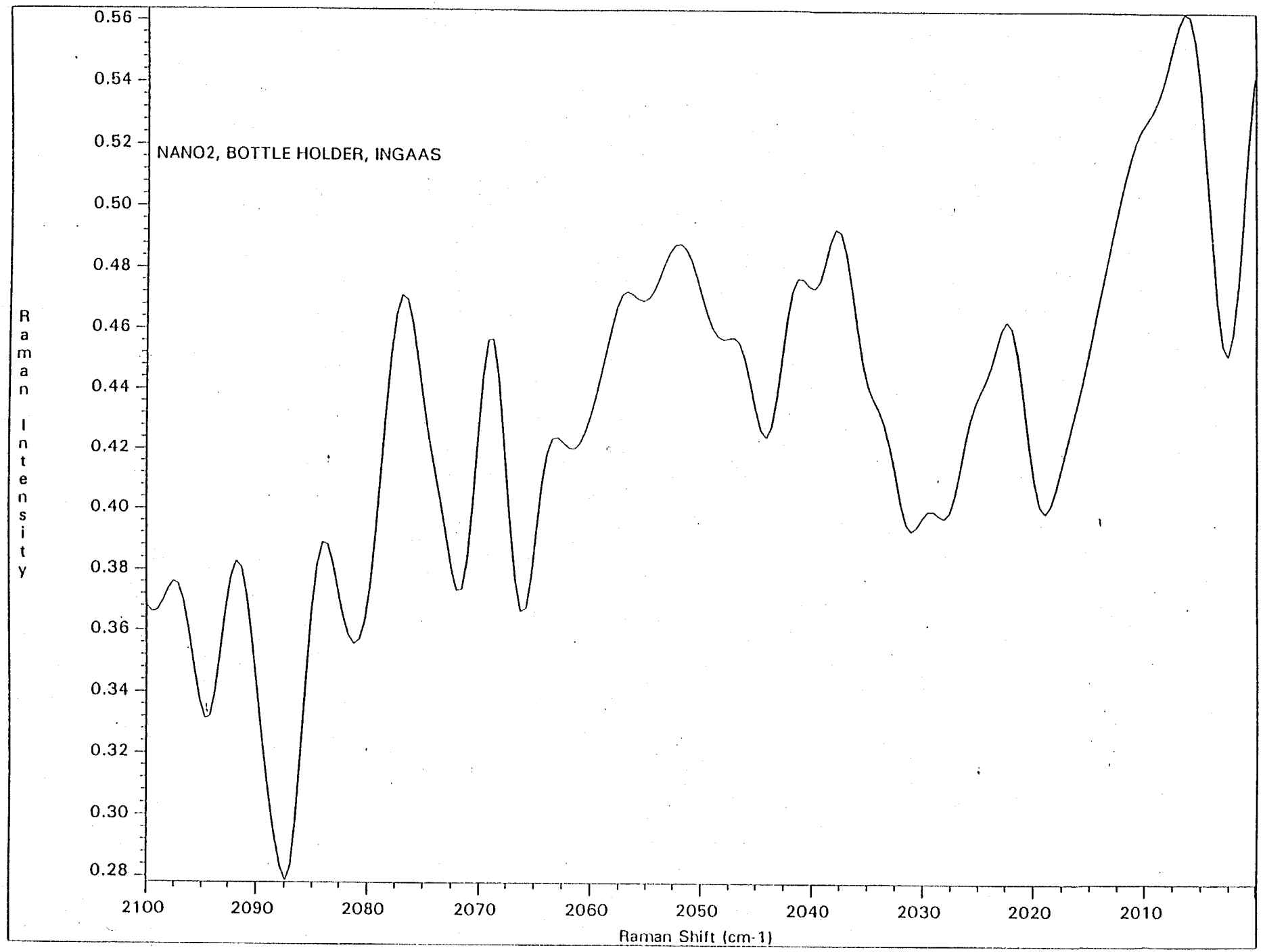

LAURIC ACID, BOTTLE DIRECT
Raman Intensity
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2000
1800
1600
1400
1200
1000
800
600
400
200
Raman Shift (cm-1)

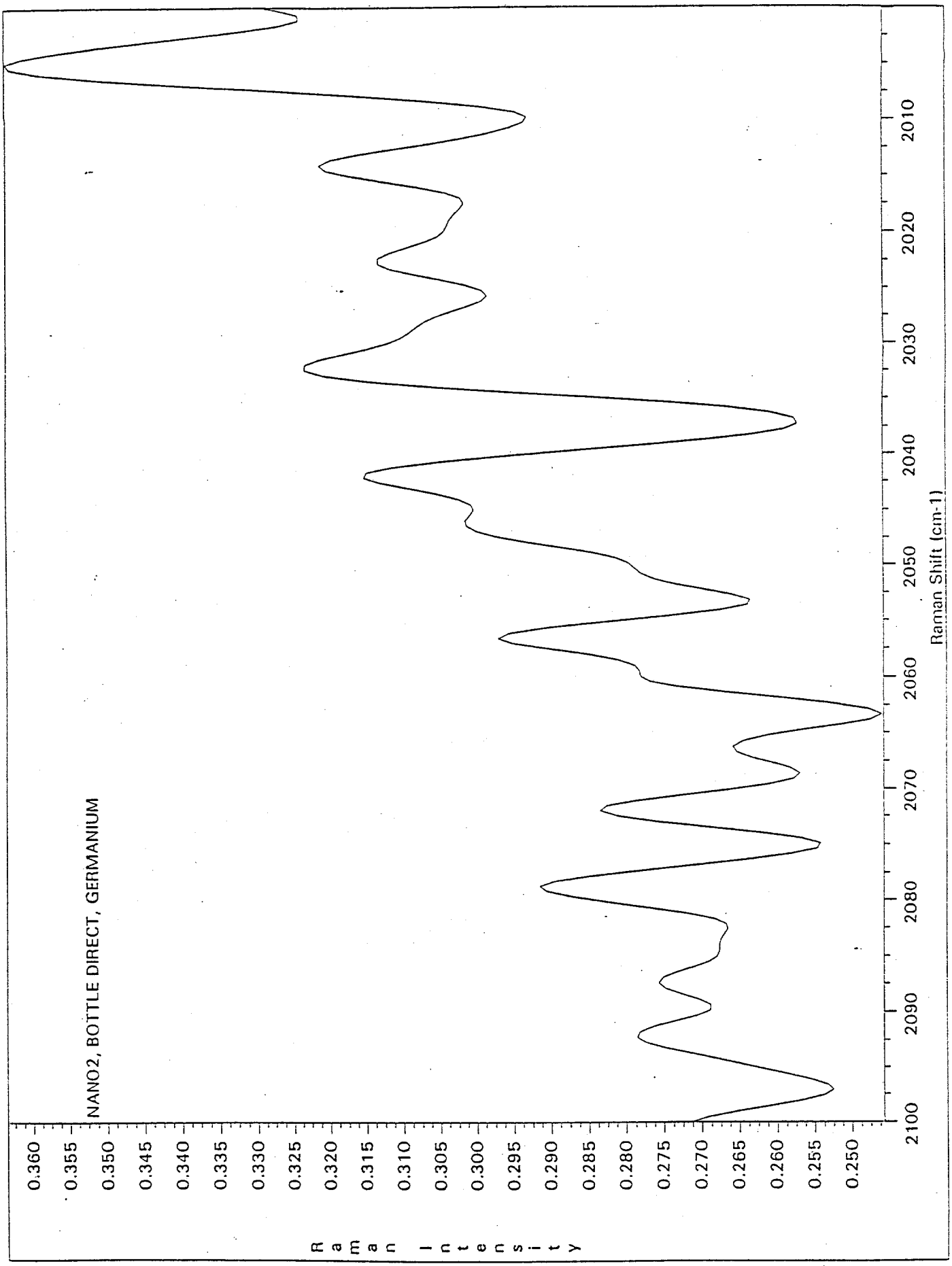

IDA, RAMAN MICROPROBE
Raman Intensity
Raman Shift (cm-1)
0.23
0.22
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
4000
3500
3000
2500
2000
1500
1000
500

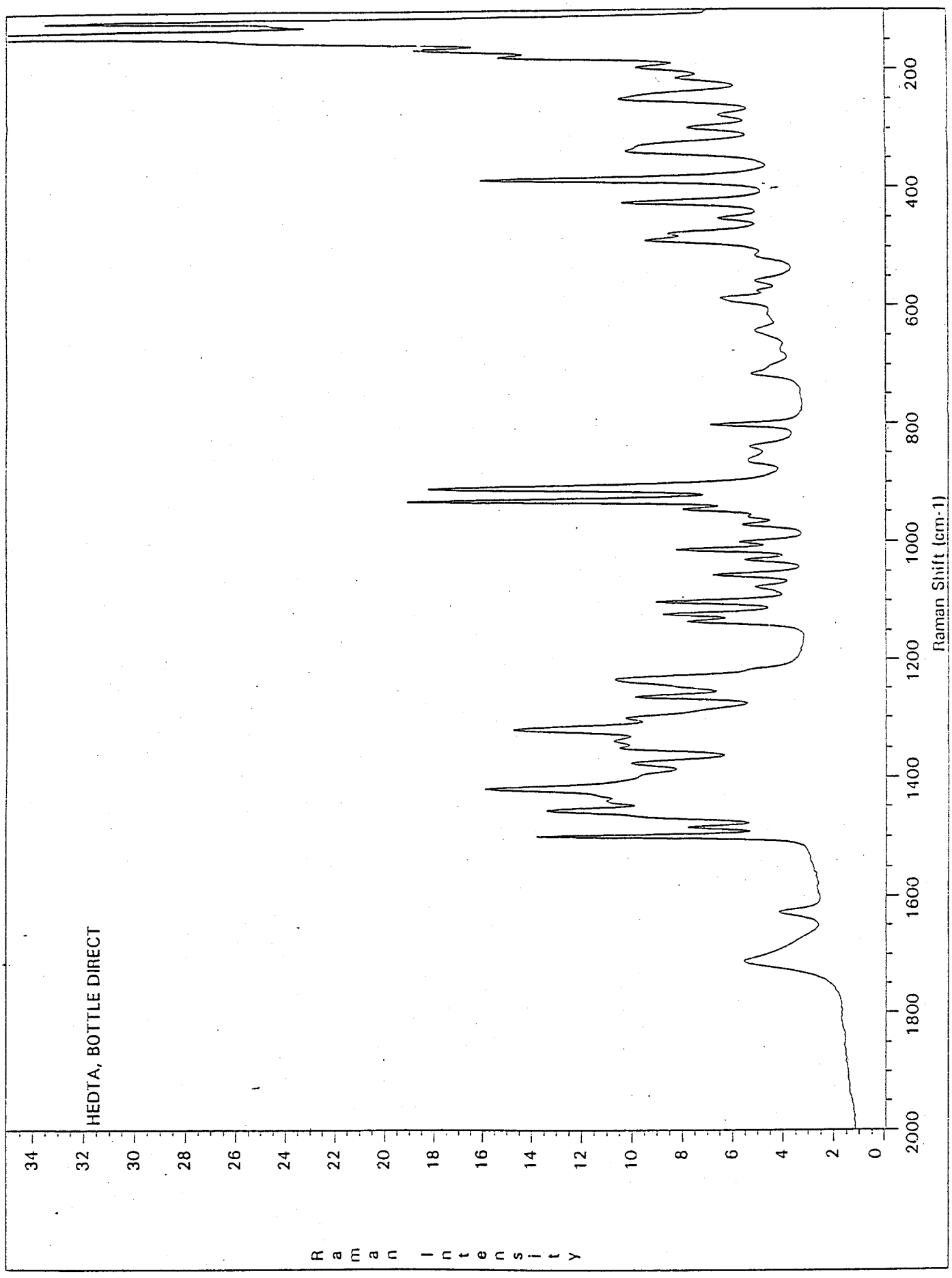

MYRISTIC ACID, INGAAS, BOTTLE DIRECT
Raman Intensity
Raman Shift (cm-1)
65
60
55
50
45
40
35
30
25
20
15
10
5
4000
3500
3000
2500
2000
1500
1000
500

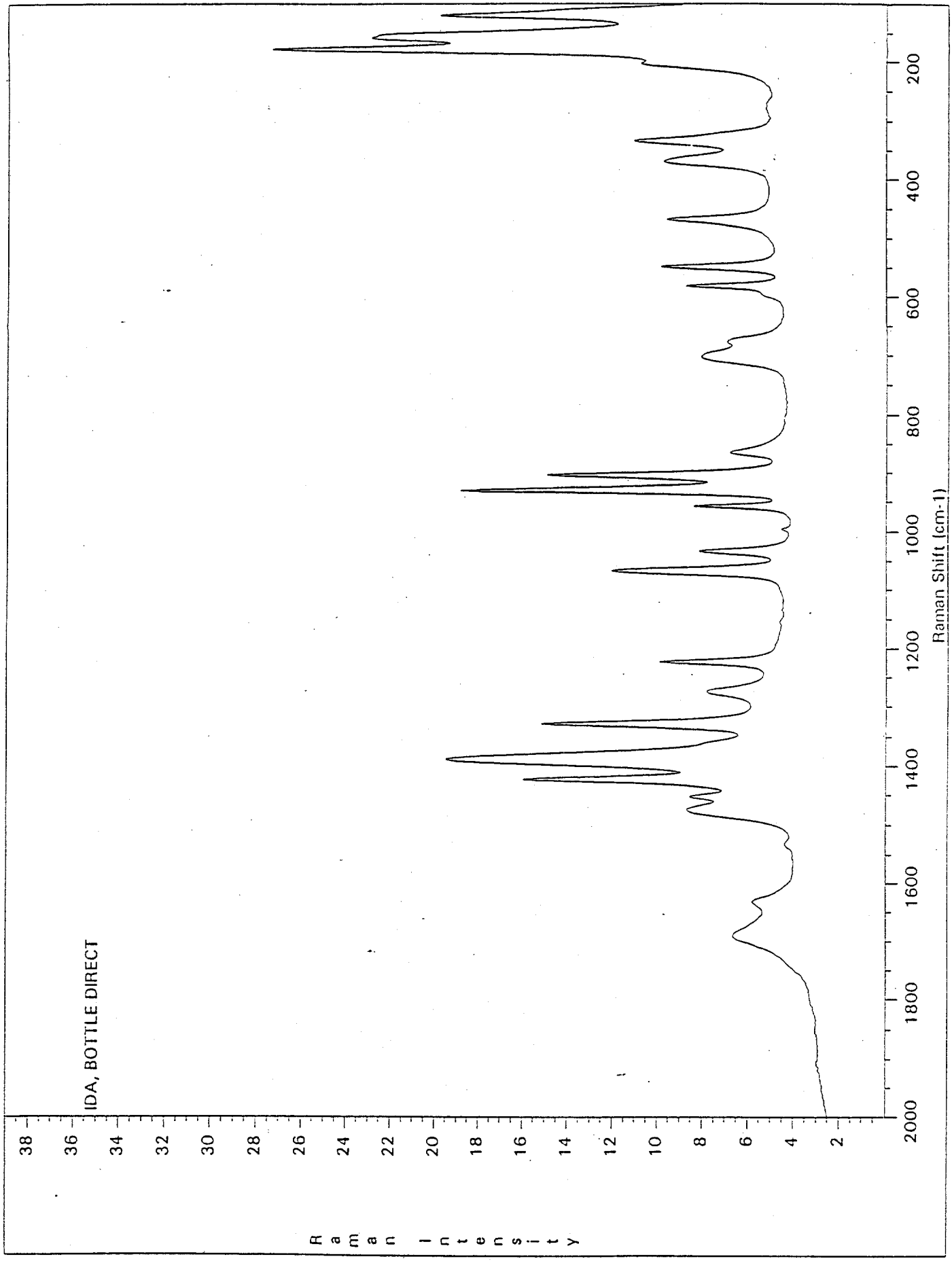

MYRISTIC ACID, INGAAS, BOTTLE DIRECT
Raman Intensity
Raman Shift (cm-1)
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
2000
1800
1600
1400
1200
1000
800
600
400
200


MYRISTIC ACID, BOTTLE DIRECT
Raman Intensity
Raman Shift (cm-1)
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
2000
1800
1600
1400
1200
1000
800
600
400
200


NANO2, BOTTLE HOLDER, INGAAS
Raman Intensity
0.56
0.54
0.52
0.50
0.48
0.46
0.44
0.42
0.40
0.38
0.36
0.34
0.32
0.30
0.28
2100
2090
2080
2070
2060
2050
2040
2030
2020
2010
Raman Shift (cm-1)


NANO2, BOTTLE DIRECT, GERMANIUM
Raman Intensity
Raman Shift (cm-1)
0.360
0.355
0.350
0.345
0.340
0.335
0.330
0.325
0.320
0.315
0.310
0.305
0.300
0.295
0.290
0.285
0.280
0.275
0.270
0.265
0.260
0.255
0.250
2100
2090
2080
2070
2060
2050
2040
2030
2020
2010


HEDTA, BOTTLE DIRECT
Raman Intensity
Raman Shift (cm-1)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
200
400
600
800
1000
1200
1400
1600
1800
2000


IDA, BOTTLE DIRECT
Raman Intensity
Raman Shift (cm-1)
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
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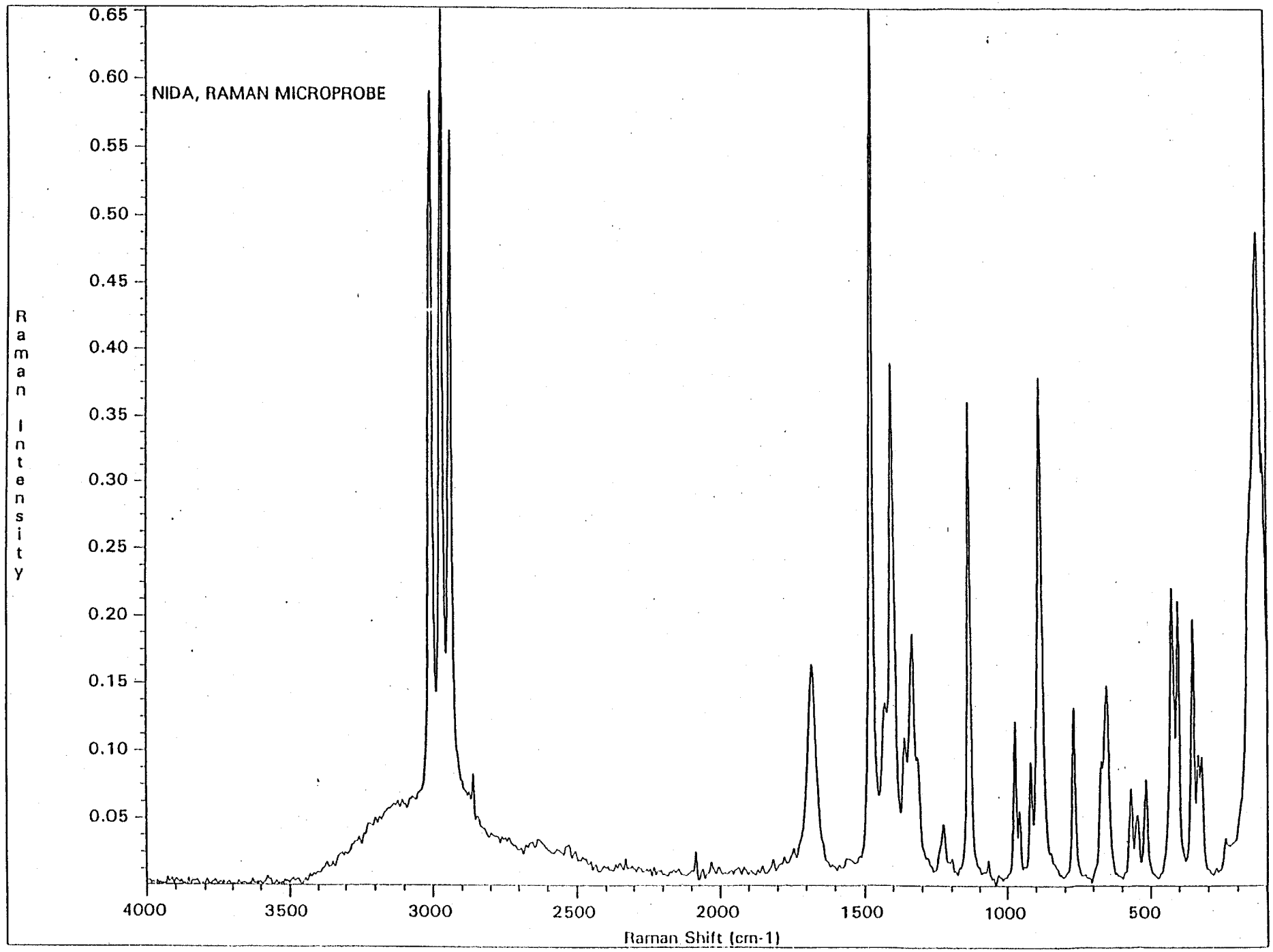
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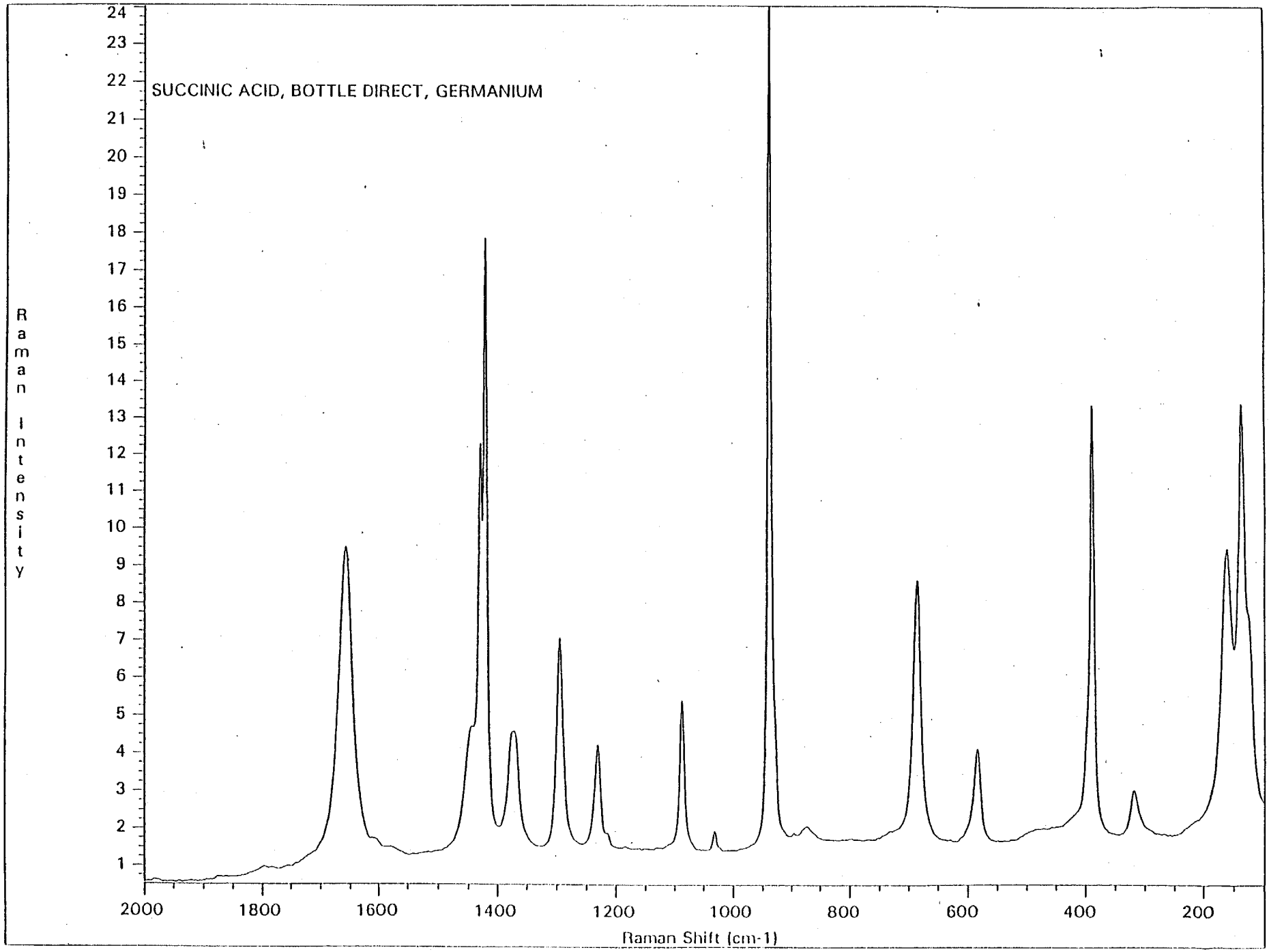
Raman Shift (cm-1)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Raman Intensity
Raman Shift (cm-1)
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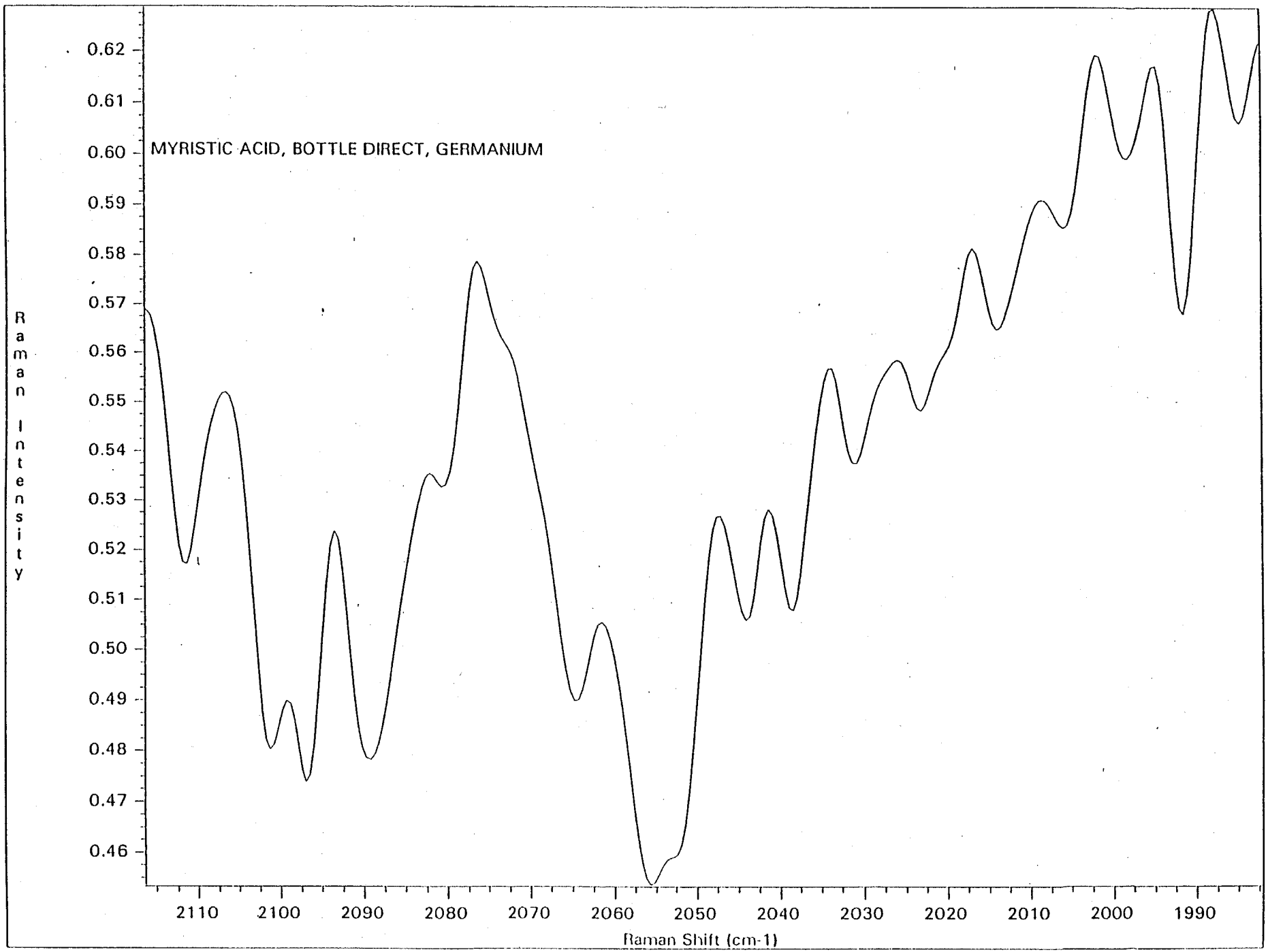
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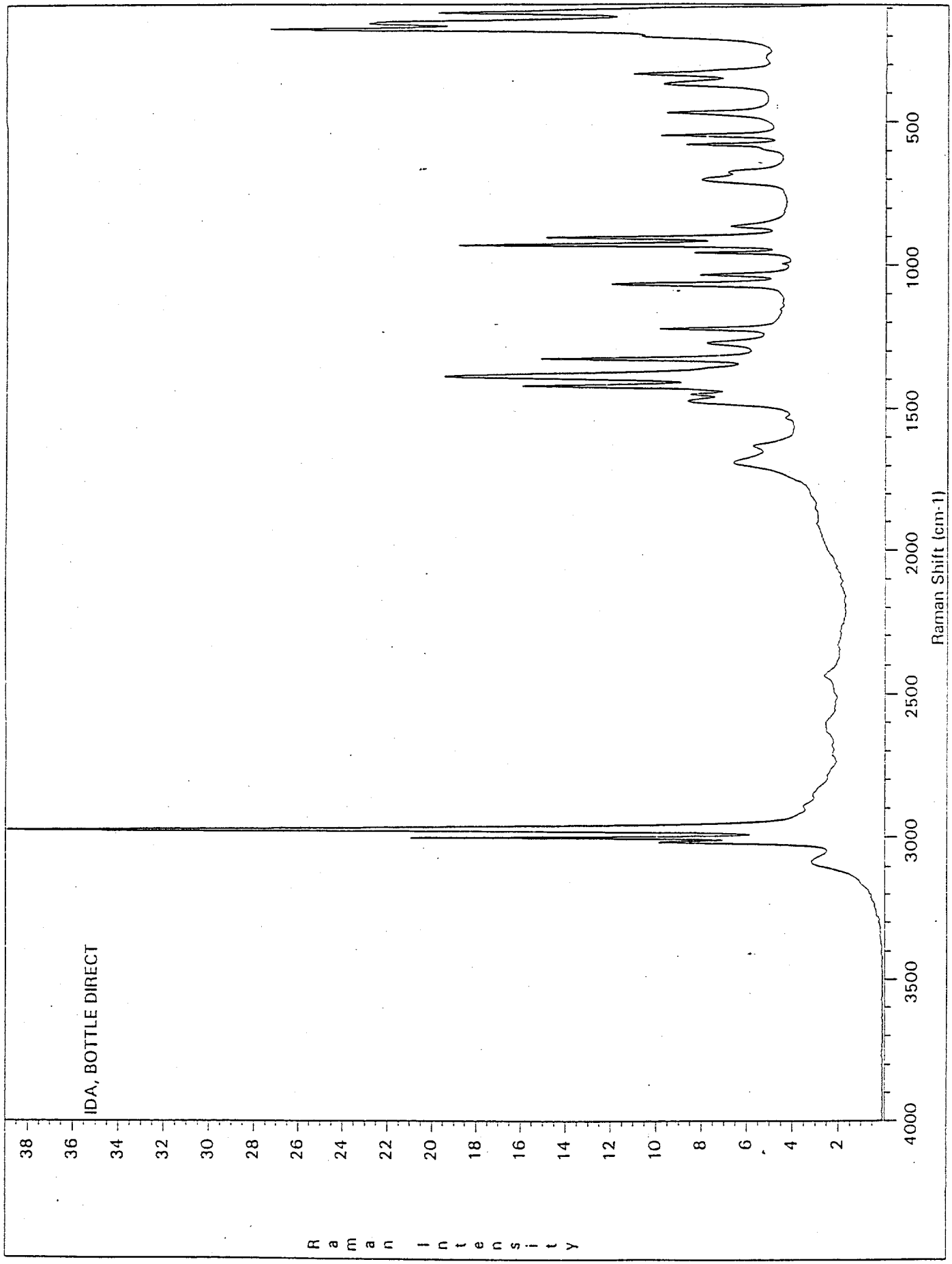
Raman Shift (cm-1)


IDA, BOTTLE DIRECT
Raman Intensity
Raman Shift (cm-1)
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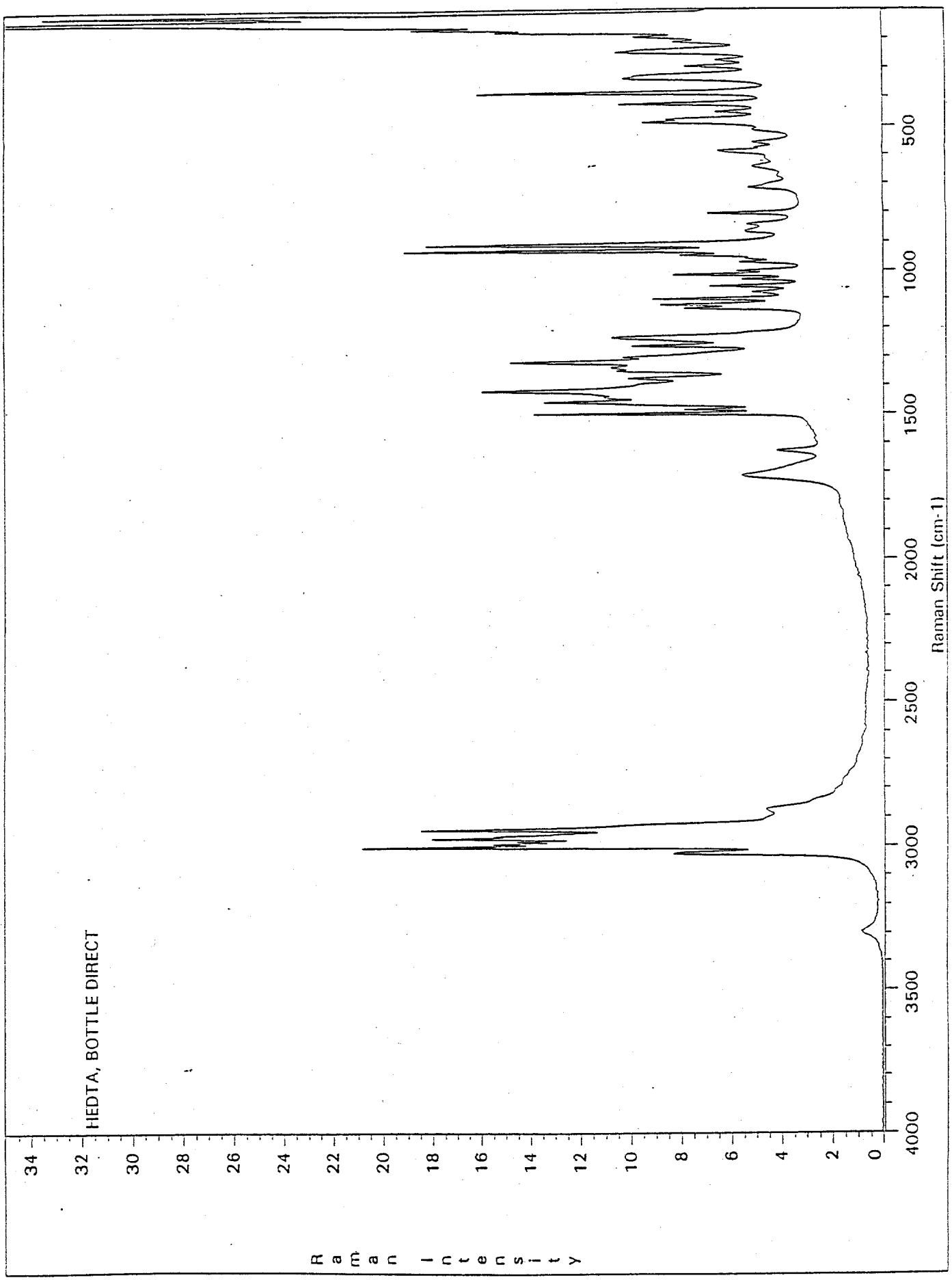
HEDTA, BOTTLE DIRECT
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Raman Shift (cm-1)
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APPENDIX C

Methods Transferred to ACL and 222-S

TEST PLAN, ORGANIC ANALYTICAL METHODS DEVELOPMENT, 6/1/94

ANALYSIS FOR LOW MOLECULAR WEIGHT ORGANIC ACIDS IN MIXED HAZARDOUS WASTE SAMPLES BY THERMOSPRAY LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY

1.0 INTRODUCTION

This test plan (TP) is for the analysis of low molecular weight organic acids (LMWA, e.g., formic, acetic, propionic, glyoxylic, etc.) in mixed hazardous waste samples by thermospray liquid chromatography - mass spectrometry (LC/MS).

2.0 RESPONSIBILITIES

2.1 Analysis Training

The cognizant scientist for this analysis implemented the method, and will assist in transferring these methods and training additional analysts. Training may include familiarity with the thermospray interface in general.

2.2 Future Development

The cognizant scientist will transfer any future modifications or improvements to the test plan described.

3.0 PROCEDURE

3.1 Objective and Scope

The objective of this TP is to describe the procedure for the analysis of LMWA in mixed hazardous waste samples by thermospray LC/MS.

3.2 Discussion

This procedure is preliminary as presented in this TP. The organic acids investigated in the development of this technique included citric, tartaric, gluconic, glyoxylic, glycolic, formic, and acetic acids. These acids, particularly glycolic acid, have proved difficult to analyze by other techniques such as derivatization GC/MS. Advantages of the technique presented in this TP include avoidance of sometimes troublesome and time-consuming derivatization and not having to remove non-volatile inorganic species prior to analysis, as long as they are soluble in the mobile phase.

Oxalic acid is not observed under these analysis conditions with either electron impact (EI) or chemical ionization (CI) mass spectrometry. Under the LC conditions utilized here with an acid exclusion column, oxalic acid elutes with nitrate and is masked by the strong signal of nitrate present in most waste samples. A more appropriate analysis method for oxalic acid would utilize an ion exchange column and atmospheric pressure chemical ionization mass spectrometry with negative ion detection.

3.3 Personnel Qualifications

Training of analysts for both sample preparation and analysis utilizing a thermospray interface for LC/MS.

3.4 Documentation

The data generated will be saved on hard disk with extra data backup in addition to a hard copy of relevant spectra and chromatograms. A log of samples analyzed will be maintained as well as instrument parameters used to collect the data.

3.5 Apparatus

3.5.1 Mass Spectrometer - HP 5988A mass spectrometer with thermospray interface, or equivalent.

3.5.2 HPLC - As an absolute minimum, an LC pump and controller with appropriate injector, valves, solvent degasser, analyte separation column, UV detector, and a printer/plotter are required. In addition, an autosampler is recommended so that samples can be injected from septum-sealed vials to help maintain control of radioactive samples.

3.5.3 HPLC Column - Bio-Rad organic acids column, Aminex Ion Exclusion, HPX-87H, 300 x 7.8 mm, or equivalent. An appropriate guard column is highly recommended.

3.5.4 Column for sample cleanup - Bio-Rad analytical grade cation exchange column. AG 50W-X8, 50-100 mesh, sodium form, or equivalent for removal of radioactivity.

3.5.5 Syringe tip filters - Gelman Acrodisc LC13, 0.45 1lm pore size filters or equivalent.

3.5.6 pH meter with pH probe covering the pH range of at least 2 to 12.

3.5.7 Volumetric flask - 25 mL

3.5.8 LC vials compatible with autosampler.

3.5.9 Solvent filtering system

3.5.10 Analytical balance for standard preparation to 0.01 mg and balance for sample weighing to 0.1 mg.

3.6 Reagents

3.6.1 Reagent water - deionized water using a deionizer with an organic removal cartridge.

3.6.2 Mobile phase - 0.001 N HCl for LC/MS. Dilute approximately 90 μL of 12 N HCl to 1 liter of H_20. Check pH should be pH 2.5. Adjust pH with dilute NH_40H if necessary.

3.6.3 Polyethylene glycol for mass spectrometric tuning and calibration .

3.6.4 pH standards - commercial pH 4, 7, 10.

3.6.5 Helium - 99.9% or better, at 0 to 7.5 psi purge gas for mobile phase.

3.6.6 Compressed air - breathing air quality, 75 psi, for autosampler operation.

3.7 Safety

3.7.1 Observe general laboratory safety rules.

3.7.2 Follow requirements of applicable RWP's.

3.7.3 Radioactive components in sample may be eluted through the entire system and into the thermospray source. Previous experience has been that radioactive components concentrate at the source area where solvent degassing occurs and do not spread to other parts of the mass spectrometer. Determine what contamination of the mass spectrometer system occurred by use of this procedure prior to instrument maintenance.

3.8 Quality Control

This method is preliminary, and as such, quality control parameters have yet to be developed.

3.9 Calibration

Quantitation can be performed with this technique once a calibration curve has been established for each LMWA to be analyzed. An internal standard, such as propionic acid, should also be utilized during sample analysis.

3.10 Calibration Standards preparation

Prepare a series of standard solutions with LMWA concentrations in the same range as expected in the waste samples. Use these solutions to prepare a calibration curve for each LMWA. If glyoxylic acid is used in the standard, this solution should be made fresh each day it is utilized to avoid errors caused by the oxidation of this acid to form oxalic acid, which occurs spontaneously in solution.

3.11 Sample Preparation

3.11.1 Radioactivity removal - A remote handling hot cell or sample preparation laboratory is utilized depending on the sample radionuclide content. Flush sample through a Bio-Rad Analytical Grade Cation Exchange column (AG 50W-X8, 50-100 mesh, sodium form) or equivalent to remove most of the radioactivity due to primary fission products in the waste. This procedure has only been tested on solutions with pH $>$ 11 and should be performed with caution at lower pH conditions as analyte may be lost.

3.11.2 Verify that the majority of the radioactivity has been removed

3.11.3 Weigh out 1 g of the cation exchanged waste sample and place in a 25.0 mL volumetric flask.

3.11.4 Adjust the pH of the sample with HCl to match the pH of the mobile phase monitored with an extended scale pH meter. This may require judicious dropwise addition of 0.5M HCl to approximate proper pH of the mobile phase. Then add 0.001 N HCl mobile phase solution to dilute solution to final 25.0 mL volume. The final solution should be approximately pH 2.5 - 4.

3.11.5 Filter an aliquot of the solution into an LC vial using a Gelman Acrodisc LC13, 0.45 μm syringe-tip filter to remove small particulates that could clog the LC column and/or the thermospray interface probe. About 20 μL of this filtered solution is used for LC/MS analysis.

3.12 LC/MS Analysis

3.12.1 Mass spectrometric and thermospray parameters are described below.

Ion source temperature 275 °C
Stem initial temperature 100 °C
Probe tip temperature 230 °C
Vapor temperature 272 °C
Filament operation in both on and off modes
Scan range 75-300 amu
Injection volume 10 μL or 20 μL depending on sample concentration
Isocratic mode

3.12.2 Calibration and tuning - Polyethylene glycol (PEG) tuning solution is used to tune up the thermospray interface and calibrate the mass spectrometer prior to unknown analysis. The standard masses of the PEG solution are given below: Verify stability of thermospray interface performance and maximize signal intensity of PEG ions.

3.12.3 Inject approximately 20 μL onto LC column connected to thermospray interface for MS detection. Start data collection as described in instrument manuals.

3.12.4 Upon completion of the analysis sequence, verify data collection. Consult system manuals to obtain printout of data and for data manipulation such as integration.

3.12.5 Verify that the data is stored on the hard disk and backup any valuable data files at the end of each day of analysis.

3.12.6 Calculate final results based on sample size and all sample dilutions and other sample manipulations performed.

3.13 Instrument Maintenance

3.13.1 Flush filtered deionized water through the thermospray probe and HPLC pump at the end of each day of operation.

3.13.2 Clean the thermospray ion source approximately once per week to remove nonvolatile chloride salts resulting from the use of HCl as the mobile phase.

TEST PLAN, ORGANIC ANALYTICAL METHODS DEVELOPMENT, 6/1/94

DETERMINATION OF CHELATORS AND THEIR DEGRADATION PRODUCTS IN MIXED HAZARDOUS WASTE SAMPLES BY DERIVATIZATION GAS CHROMATOGRAPHY-MASS SPECTROMETRY

1.0 INTRODUCTION

This test plan (TP) is for the analysis of chelators and their degradation products in mixed hazardous waste samples by gas chromatography mass spectrometry (GC/MS).

2.0 RESPONSIBILITIES

2.1 Analysis Training

The cognizant scientist for this analysis implemented the method, and will assist in transferring these methods and training additional analysts.

2.2 Future Development

The cognizant scientist will transfer any future modifications or improvements to the test plan described.

3.0 PROCEDURE

3.1 Objective and Scope

The objective of this TP is to describe the procedure for the derivatization of chelators and their degradation products in mixed hazardous waste samples for analysis by GC/MS.

3.2 Discussion

This procedure is preliminary as presented in this TP. Important variables have been evaluated as well as alternative derivatization procedures. The procedure outlined in this TP has performed the best to date on the actual waste samples analyzed. However, due to the variability in the mixed waste samples, modifications to the sample preparation and/or derivatization procedure may be necessary.

This derivatization procedure with BF3/methanol will methylate carboxylic acids but not hydroxy groups in organic analytes. This procedure may also result in the lactone formation in the case of HEDTA. In addition this procedure is not reproducible for the derivatization of the symmetrical ethylenediaminediacetic acid.

This derivatization GC/MS procedure is very useful in identifying major organic components present in the waste samples including citric acid, nitriloacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), (2hydroxyethyl)ethylenediaminetetraacetic acid

(HEDTA), and ethylenediaminetriacetic acid (ED3A). Other organic acids that are artifacts of the waste are also readily derivatized with BF3/methanol, including succinic and oxalic acids.

In the preparation of calibration standards it was noted that NTA and its salts were found to be difficult to dissolve in water/NaOH solutions. Further testing will be done to resolve this issue. It may be possible to dissolve NTA in strong basic solutions (pH 13) and then dilute to volume with H_20.

IDA was found to easily decompose, assumed to be saponification, if the extraction solution ever reached pH $<$ 7. Hence, the quenching solution was modified to pH 9 - 9.5 so that final extraction was at pH 7 - 7.5. A titration of the BF_3/MeOH reagent vs. KH_2PO_4/NaOH solution is recommended to approximate the final volumes that will give the best results.

Quantitative data on HEDTA must be interpreted with caution. The HEDTA response is apparently only due to the lactone form and not the free hydroxide species, based on mass spectrometric data.

3.3 Personnel Qualifications

Training of analysts for both sample preparation and analysis utilizing GC/MS. The mass spectrometer operator should be capable of performing electron impact GC/MS as well as chemical ionization GC/MS.

3.4 Documentation

The data generated will be saved on hard disk, backup and a hard copy will be provided. A log of samples injected into the GC/MS will be maintained as well as instrument parameters used to collect data.

3.5 Apparatus

3.5.1 Mass Spectrometer - HP 5988A mass spectrometer with electron impact (El) and chemical ionization (Cl) capabilities with GC/MS, or equivalent.

3.5.2 Gas Chromatograph with a fused silica capillary column: DB-5, 30m x 0.25 mm i.d., 0.25 μm film thickness (J & W Scientific), capable of splitless injection.

3.5.3 Vortex mixer to stir solutions.

3.5.4 Reactivial heating block.

3.5.5 Reaction vials (VWR Scientific or equivalent).

3.5.6 pH meter with pH probe covering the pH range of at least 2 to 12.

3.5.7 Test tubes

3.5.8 Mechanical stirrer and stir bars.

3.5.9 Solvent filtering system.

3.5.10 Balance for sample weighing from mg to g capacity.

3.6 Reagents

3.6.1 Reagent water - deionized water using a deionizer with an organic removal cartridge.

3.6.2 Boron trifluoride/methanol 12% w/v (Aldrich) for sample derivatization .

3.6.3 Perfluorotributylamine (PFTBA) for mass spectrometry calibration and instrument performance assessment.

3.6.4 Chloroform (Reagent Grade) Burdick and Jackson or equivalent.

3.6.5 Buffer solution of 1 M KH_2PO4 which has been pH adjusted to 9.0 - 9.5 with NaOH.

3.6.6 NaOH for pH adjustment.

3.6.7 pH standards - commercial pH 4, 7,10.

3.6.8 Helium - 99.9% or better, for GC carrier gas.

3.6.9 Compressed air - breathing air quality, 75 psi, for autosampler operation.

3.6.10 Methane and isobutane for Cl reagent gases.

3.6.11 Nitrogen - for blow down procedure for solvent evaporation.

3.6.12 Anhydrous Na_2SO_4

3.7 Safety

3.7.1 Observe general laboratory safety rules.

3.7.2 Follow requirements of applicable-RWP's.

3.8 Quality Control

This method is preliminary, and as such, quality control parameters have yet to be developed. Currently there is no internal standard fully characterized and ready for implementation. External standards may be used until internal standards are developed and tested. Internal standards currently under development include d^4-EDTA and d^4- succinc acid. When feasibility of these compounds for use as internal standards have been demonstrated, this capability will be transferred for addition to this test plan.

3.9 Calibration Standards Preparation

3.9.1 A standard solution is prepared for use in producing response curves for the analytes of interest. Prepare a stock solution containing a known amount (~5 mg/ml) in 0.1 M NaOH of each of the following chelators: succinic acid, IDA, NIDA, citric acid, NTA, EDTA, HEDTA (or similar based on what is expected in sample solutions). Concentrations of chelators in standard solution should be greater than expected concentrations in sample solutions.

3.9.2 Place a known aliquot (2-5 mL) of standard solution in a 5 mL Reactivial and blow down to dryness as described in step 3.10.2.

3.9.3 Derivatize this standard simultaneously with the samples following steps 3.10.3 through 3.10.10.

3.10 Sample Preparation

Depending on radioactivity levels, steps 3.10.1 through 3.10.9 may have to be performed in a hot cell or glove box. Check with RPT and RWP before proceeding.

3.10.1 Weigh out 2 grams of the solids sample. Add 20 mL of doubly-distilled deionized water and stir overnight.

3.10.2 Filter solutions with a 0.45 Am syringe filter, or equivalent. Some solutions with high solids content may required centrifugation prior to filtering. Place known aliquot of aqueous portion (2-5 mL) in a 5 mL Reactivial and evaporate to dryness with a steady stream of dry nitrogen and heat up to 70°C. To achieve complete dryness, it may be necessary to manipulate the sample, i.e. tilt vial to spread out thickened salts onto vial wall.

3.10.3 After complete dryness has been achieved, approximately 2 mL of 12% BF_3/methanol is added to the Reactivial and the sample is heated to 100°C for 1 hour.

3.10.4 Cool the sample and then add 1 mL of chloroform.

3.10.5 Transfer solution to test-tube containing 5 mL of 0.1 M KH2PO4 adjusted to pH 9.0 - 9.5 with NaOH.

3.10.6 Rinse out Reactivial with another 1 mL of chloroform and add to the test tube.

3.10.7 Vortex sample and allow the aqueous and chloroform layers to separate.

3.10.8 Decant off the aqueous layer from the top and discard (must be monitored for radioactivity before disposal). The bottom chloroform layer (~2 mL) contains the derivatized organics for analysis.

3.10.9 Record volume of solution through the remainder of the sample preparation steps. Quantification is based on the assumption that the chelators are now contained in the 2 mL

chloroform layer. Any extra dilutions, concentrations or filtering that affect this final volume must be taken into account when performing quantitative calculations.

3.10.10 Add 100 mg - 200 mg anhydrous Na_2SO_4 to collect entrained water. Transfer the dried solution to a clean vial.

3.10.11 At this point the chloroform layer should have less than 5% of the original radioactivity of the original sample. Verify this with the RPT and then remove sample from hot cell and proceed with GC/MS analysis.

3.11 GC/MS Analysis

3.11.1 Mass spectrometric and GC parameters are described below. Record all instrument parameters in laboratory notebook.

Ion source temperature 200 °C
injector port temperature 250 °C
Interface temperature 250 °C
GC oven temperature program 50°C for 1 min., 8°C/min to 300°C, hold at 300°C for 5 min. GC operated in the splitless mode Electron Impact (EI)
Scan range 50-500 amu
Electron energy 70 eV

Chemical Ionization (Cl)
Isobutane was used for reaction gas
positive ion mode scan range 70-500 am
negative ion mode scan range 100-600 with ion source temperature 250°C.

3.11.2 Calibration and tuning - Use Perfluorotributylamine (PFTBA) to tune and calibrate the mass spectrometer prior to unknown analysis. All calibration results and instrument parameters should be documented in the laboratory notebook.

3.11.3 Once calibration and system performance have been completed and documented, response curves can be generated with the standard solution. Make a series of dilutions of the derivatized standard solution with chloroform. If concentration ranges of the chelators present in the sample solutions is unknown, perform at least the following dilutions of the stock solution (assuming the stock solution concentration is 2 - 5 mg/mL): 1:1, 1:5.1:10.1:25.1:50 and 1:100.

3.11.4 Inject approximately 1 μL of each of the standard dilutions onto the GC column for GC/MS analysis. Start data collection as described in instrument manuals. If autosampler is available, then a batch run can be setup as described in manuals.

3.11.5 Prepare response curve for each analyte in the standard solution by plotting area of GC peak vs. μg methylated chelator injected.

3.11.6 Inject approximately 1 μL of unknown sample onto GC column for GC/MS analysis. Start data collection as described in instrument manuals. If autosampler is available, then a batch run can be setup as described in manuals.

3.11.7 Upon completion of the analysis sequence, verify data collection. Consult system manuals to obtain printout of data and for data manipulation such as integration and library searching.

3.11.8 Verify that the data is stored on the hard disk and backup any valuable data files at the end of each day of analysis.

3.11.9 Calculate final results based on sample size and all sample dilutions and other sample manipulations performed. Use response curve to obtain quantitative information.

APPROVALS:

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