ORGANIC ANALYSES OF MIXED NUCLEAR WASTES

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ABSTRACT

Analytical methods are being developed at Battelle's Pacific Northwest Laboratory for the organic analysis of nuclear wastes. In this study our laboratory analyzed the organic content of three commercial wastes and an organic-rich, complex concentrate waste. The commercial wastes contained a variety of hydrophobic and hydrophilic organics, at concentrations ranging from nanomolar to micromolar. Alkyl phenols, chelating and complexing agents, as well as their degradation products, and carboxylic acids were detected in the commercial wastes. The complex concentrate waste contained chelating and complexing agents, as well as numerous degradation products, at millimolar concentrations. To date, 75.1% of the complex concentrate waste's total organic carbon content has been identified. The presence of chelator fragments in all of the wastes analyzed, occasionally at elevated concentrations, indicates that organic diagenesis, or degradation, in nuclear wastes is both widespread and quite vigorous.

INTRODUCTION

Nuclear waste management currently faces numerous challenges. Permanent waste disposal technologies for low- and high-level wastes currently being developed are slated for implemention in the near future. Environmental legislation such as the Resources Conservation and Recovery Act (RCRA) of 1976 is being applied to nuclear operations, including government operations, with increasing vigor. Such activities have defined and highlighted numerous criteria which need to be addressed before the wastes can be permanently disposed. Certainly, one of the most important criteria is thorough waste characterization, particularly of mixed nuclear wastes, i.e. wastes containing both radionuclides and hazardous chemicals. Numerous hazardous chemicals consisting both of inorganic and organic species, have been targeted by federal and state regulatory agencies.

Our group at Battelle's Pacific Northwest Laboratory (PNL) is currently involved in analyzing the organic content of nuclear wastes from myriad sources, ranging from commercial to defense wastes. Based on our experience and the literature, it is clear that organics have been used extensively in nuclear operations, e.g. waste reprocessing, and continue to be used widely as solvents, degreasing agents, decontamination agents, flocculating agents, etc (1-5). The presence of certain organics in nuclear wastes may certainly complicate waste management efforts. For example, some compounds may be toxic or may enhance subsurface transport of radionuclides (6-12). Such concerns have prompted studies to characterize the organic content of nuclear wastes prior to their permanent disposal.

In this report we describe the organic analysis of two classes of nuclear waste: three commercial wastes and an organic-rich complex concentrate waste. For the commercial wastes, the goal of our analyses is to identify organics which might complex or chelate radionuclides, thereby potentially enhancing their leachability and subsurface transport through soils. For the complex concentrate waste, our goal is to completely characterize its organic content, relative to total organic carbon (TOC), in support of waste solidification efforts.

EXPERIMENTAL

Samples

Three wastes were obtained from commercial nuclear power reactors. One of the wastes, the PWR waste, is a boric acid concentrate waste obtained from a pressurized water reactor (PWR). Two of the wastes, BWR Wastes No.1 and No.2, are evaporator concentrates of liquid wastes produced during the regeneration of ion-exchange resins used to purify process water in a boiling water reactor (BWR). Such liquid regeneration wastes are evaporated to reduce volume. All three wastes consisted of mixed liquid and solid phases, necessitating special sample preparation procedures.

The complex concentrate waste was generated during numerous reprocessing campaigns, in which organic species such as chelating agents were used to improve the waste's properties, e.g., extraction of heat-producing radionuclides. The result is an organic-rich (44 g TOC/L) radioactive waste (1 Ci/L). Because of its high radioactivity, the waste was diluted 500-fold with distilled water before organic analysis was undertaken. Consequently, the sample analyzed was a clear solution, with no solids or colloidal material.

Sample Preparation

Commercial Wastes: These waste samples were mainly liquid but appreciable amounts of solid residue were also present at room temperature. To insure the best analyses possible, the liquid and solid phases were analyzed separately. The PWR waste existed as separate liquid and solid phases at room temperature, whereas the BWR wastes existed as suspensions that required centrifugation. For the PWR waste, 20 mL of the liquid phase and 6g of the solid residue were subsampled for analysis. For the BWR No.1 waste, 4 mL of liquid phase and 2g of the centrifuged solids were subsampled for analysis. For the BWR No.2 waste, 4 mL of the liquid phase and 6g of the centrifuged solids were subsampled for analysis.

The solid phase of each commercial waste had to be extracted prior to final sample preparation.

Each solid phase was extracted with a specific amount of Milli-Q purified water, 30-60 mL, for 48h with magnetic stirring. The extraction system was maintained at pH 11 throughout the extraction. The alkaline extract was then separated from the extracted waste by centrifugation.

Each liquid phase and alkaline extract of the wastes was extracted with chloroform to remove any hydrophobic organics which might be present in the wastes. Each hydrophobic organic extract was then concentrated under N_2 at room temperature to 100 μL, in preparation for gas chromotography (GC) and combined GC-mass spectrometry (GC-MS) analysis.

The final stage of sample preparation entailed derivatization of the wastes' hydrophilic organics. Each alkaline extract of the wastes was concentrated to near dryness by rotary vacuum evaporation at 50°C. Each concentrated extract and liquid phase of the wastes was then serially transferred to a 5 mL reaction vial and completely dried under N_2 at 50°C. Each sample residue was then methylated in a sealed reaction vial with 1 mL of BF_3/methanol (14% w/v) at 100°C for 40 min. After cooling, 1 mL of chloroform was added, the mixture was transferred to a test tube containing 3 mL of 1M KH_2PO_4 buffer solution (pH 7) with a 0.2 mL chloroform rinse and vortexed. Part of the chloroform layer (0.6 mL), which contained the methylated hydrophilic organics, was then pipetted into a 1 mL reaction vial and analyzed by GC and GC-MS.

GC Analysis: GC analyses were performed on a Hewlett-Packard 5880 gas chromatograph equipped with a 60 m x 0.25 mm I.D. fused silica capillary column coated with a 0.25 μm film of SE-52 and a splitless injection system. From an initial value of 40°C, the column temperature was programmed at 20°C per minute for 3 minutes to 100°C, followed by 8°C per minute for 25 minutes to 300°C, and finally maintained isothermally at 300°C for 10 minutes.

GC-MS Analysis: GC-MS analyses were performed on a Hewlett-Packard 5985 GC-MS instrument in the electron-impact (70-eV) mode. The gas chromatograph on the HP 5985 instrument was equipped with a 60 m x 0.25mm I. D. fused silica capillary column coated with a 0.25 μm of SE-54; the column was programmed from 40°C to 300°C at 5°C per minute, where it was maintained isothermally for 8 minutes. A splitless injection system was used to introduce the sample onto the GC-MS instrument. A mass range of 50 to 400 amu was scanned every 1.0 sec by computer (HP-7920 Large Disc Drive).

GC/FTIR: Analyses were performed on a Nicolet 60 SX FTIR instrument (Nicolet Analytical Instruments; Madison, WI) equipped with a Nicolet 1280 computer and interfaced to an HP 5840 GC. The GC was equippped with a wide-bore, fused silica capillary column (10 m x 0.53 mm ID coated with a 1.5 μm film of OV-17) and a splitless injection system, which was maintained at 200°C. The GC column temperature was programmed from 40°C to 250°C at 30°C per min. Helium was used as the carrier gas at 5 mL per min. The temperature of the GC/FTIR interface was maintained at 250°C. The FTIR instrument was operated at a resolution of 8 cm-1 with a scan rate of 2 scans per sec over a wavenumber range of 5000 to 700 cm-1. The temperature of the light pipe was maintained at 200°C.

Quantitation: Individual organics identified by GC-MS analyses were quantitated by GC with flame ionization detection (FID), using internal and external standards identical to or representative of compounds identified by GC-MS. After methylation a specific amount (1-2 μL) of each standard was co-injected with each sample to confirm GC-MS identifications. For quantitation, each standard was also injected onto the GC before and after sample analyses. Response factors, typically expressed as nanograms of analyte per GC area counts, were calculated for each standard under conditions identical to those of the sample analyses.

Materials

Standards: The standards used in the GC analyses were purchased from Aldrich Chemical Company (Milwaukee, Wisconsin), United States Pharmacopeial Convention, Inc. (Rockville, Maryland) and Sigma Chemical Company (St. Louis, Missouri).

Chromatographic Columns: The SE-52 and SE-54 silica capillary columns used in the GC and GC-MS analyses were purchased from J&W Scientific, Inc. (Rancho Cordova, California).

Reagents, Solvents, and Glassware: The BF_3/Methanol (14% w/v) used in the methylation reaction was purchased from Regis Chemical Company (Morton Grove, Illinois). All of the solvents used in the organic analyses were redistilled-in-glass solvents purchased from Burdick and Jackson Laboratories, Inc. Deionized water, prepurified for laboratory use, was further purified on a Milli-Q system (Millipore) containing two ion exchange resins and two charcoal filters. All glassware was acid cleaned in a hot solution of sulfuric acid/nitric acid (4:1 v/v).

RESULTS AND DISCUSSION

Commercial Wastes

Both the hydrophobic and hydrophilic organic extracts of the commercial wastes contained detectable organics. However, only the liquid phase of the PWR waste contained any detectable hydrophilic organics.

Hydrophobic Organics: Quite a variety of hydrophobic organics were identified in the commercial wastes, particulary the BWR wastes, and at relatively high parts per million (ppm) concentrations (Table I). The two most abundant classes of compounds were a family of alkylphenols and two families of alkylphenyl phosphate esters. These two classes were most representative of the BWR wastes but a number of alkylphenols were also detected in the solid phase of the PWR waste. Such compounds are typically used as hydraulic fluids and plasticizers in industry. The liquid portion of the PWR waste contained only two identifiable hydrophobic organics, but at appreciable concentrations.

The two BWR wastes differed in that the solid portion of BWR No.1 waste contained most of the organics (149.9 ppm versus 49.1 ppm for the solid and liquid, respectively), whereas the liquid portion of BWR No.2 waste contained most of the organics (109 ppm versus 56.3 ppm for the liquid and solid, respectively). All of these observations point to the need for performing thorough source-term characterization on wastes. Even related wastes may vary fundamentally with respect to their chemical content, making simplistic predictions about leachability, etc., of the processed waste difficult, if not meaningless.

Hydrophilic Organics: Quite a variety of hydrophilic organics were identified in the commercial wastes (Table II). Nothing is reported for the solid phase of the PWR waste because no organics were identified in this phase. Several classes of hydrophilic compounds are represented

TABLE I

Hydrophobic Organics in Commerical Nuclear Wastes from Nuclear Power Reactors[a]

	Concentration (ppm)[b]					
	PWR Waste		BWR Waste No.1		BWR Waste No.2	
	Liquid	Solid	Liquid	Solid	Liquid	Solid
Alkyl Phenols						
Cresol (Methylphenol)		1.5	3.2	25.8	4.3	5.9
Dimethylphenols (3)[c]		11.1	1.3	14.4	0.7	16.2
Ethylphenol		7.1	3.9	8.8	1.7	9.5
C_2-phenols (6)[c]			10.8	89.7	16.3	17.2
2,6(di-t-butyl)4-ethylphenol		0.3		1.3		0.5
4-methyl,2-nitrophenol				6.4		1.6
Ethylnitrophenols (3)[c]						
Phosphate Esters						
Di(alkylphenyl)methylphosphates (3)[c]					73.2	
Tri(alkylphenyl)phosphates (22)[c]			15.4		11.1	2.9
Phthalate Esters						
Dioctylphthalate	33.2					
Dimethylphthalates (2)[c]			14.4		1.5	
Alkylphthalate			0.1	1.8	0.2	1.2
Hydroxybenzaldehyde	46					
N-(phenyl,methyl)amine				0.8		
Benzene Sulfonamide				0.9		0.8
Polyethylene glycol						0.5

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[a] Wastes obtained from a pressurized water reactor (PWR) and a boiling water reactor (BWR)

[b] No entry indicate compound is below detection level (0.1 ppb)

[c] Number of compounds identified

in the commercial wastes, consisting mainly of organic acids.

Perhaps the most interesting class of organics identified in the commercial wastes are the chelating agents and a related class of organics, the chelator fragments. Their structures are depicted in Fig. 1. These organics are particularly abundant and diverse in the PWR waste, ranging from 0.1 μM to 22.5 μM. Of these organics only EDTA is used commercially in nuclear operations. Such organics bind to certain radionuclides and heavy metals quite strongly, potentially enhancing their leachability by groundwater from buried wastes and facilitating their transport in soil (8-12).

The other nine EDTA-related organics, identified in our laboratory by GC-MS and GC-FTIR analyses, are undoubtedly derived from the chemical, radiolytic and/or thermal degradation of source-term organics like EDTA, which were originally used in the nuclear operations which generated these wastes. Of these nine chelator fragments, we have identified the structure of five fragments, ED3A, IDA, HEIDA, MeEDD'A, and MeEDDA; the remaining four species are only partially characterized (see Table II). The PWR waste was comparatively rich in ED3A and the other chelator fragments, presumably because the chemical/radiolytic decomposition of EDTA in the PWR waste was much more vigorous compared to the BWR wastes. Most of the chelating agent content in BWR No.1 waste, which was quite appreciable at 70.7 ppm, consisted of undegraded EDTA (68.9 ppm). BWR No.2 waste did not contain detectable levels of chelating agents.

The chelator fragments identified are capable of binding to metals and radionuclides to varying extents. In some cases the association may be quite strong. For example, the hydroxyethyl moeity of HEIDA, HEDTA, etc., reportedly has a particularly high affinity for complexing Fe(3+) (3). It is also known that the higher-valence-state chelates of EDTA, e.g. Fe(3+)-EDTA, may decompose autocatalytically at higher temperatures (3). HEIDA and IDA are known thermal decomposition products of EDTA. The binding affinity of the hydroxyethyl moeity may well explain the autocatalysis of Fe(3+)-EDTA solutions. Thus, the chelating capacity of solutions of chelating agents at higher temperatures may be due primarily to chelator fragments and not the chelating agents themselves.

A number of other hydrophilic organics identified in the commercial wastes also bind to radionuclides fairly strongly. Compounds such as citric acid, oxalic acid and glycolic acid are commonly used as complexing agents in nuclear operations (1,5). Citric acid was relatively abundant in the PWR waste at 7.1 ppm. A related compound, methanetricarboxylic acid, was even more abundant at 7.8 ppm. This compound is not available commercially and is, therefore, presumably a degradation product derived from citric acid. It is likely that such compounds can also solubilize and mobilize radionuclides unless precautions are taken, e.g., destruction, pH adjustment, etc.

The relative distribution of organics between the liquid and solid phases of the wastes varied considerably. The solid phase of BWR No.1 waste

Table II
Hydrophilic Organics[a] in Commercial Nuclear Wastes[b] from Nuclear Power Reactors[c]

	Concentration (ppm)[d]				
	PWR Waste[e]	BWR Waste No. 1		BWR Waste No. 2	
	Liquid	Liquid	Solid	Liquid	Solid
Chelating Agents[a]					
Ethylenediaminetetraacetic Acid (EDTA)	11.2	2.1	66.8		
Chelator Fragments					
Ethylenediaminetriacetic Acid (ED3A)[f]	22.5	1.8			
Iminodiacetic Acid (IDA)	20.4				
N-(2-Hydroxyethyl)iminodiacetic Acid (HEIDA)[g]	0.8				
N-Methylethylenediamine-N,N′-diacetic Acid (MeEDD′A)[h]	6.4				
N-Methylethylenediamine-N′,N′-diacetic Acid (MeEDDA)[h]	2.8				
Unknown Chelator Fragments	22.0				
Tricarboxylic Acids[a]					
Methane Tricarboxylic Acid	7.8				
Citric Acid	7.1	1.8		0.4	
Dicarboxylic Acids[a]					
e.g. Oxalic Acid	0.43	66.7	207.2	31.0	1.4
Monocarboxylic Acids[a]					
(e.g. Hexadecanoic Acid)		3.1	151.5		4.5
Oxygenated Acids[a]					
(e.g. Glycolic Acid)		16.2	141.4	18.6	6.9
Aromatic Acids[a]					
(e.g. Benzoic Acid)		17.4	44.2	3.6	
Ketones					
(e.g. 4-Methoxybenzaldehyde)		1.4		1.4	3.6

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[a] Methylated (BF_3/methanol, acids identified as methyl esters); [b] PWR waste existed as separate liquid and solid (~30%) phases at room temperature: (63% liquid, 37% solid; BWR No. 2: 47% liquid, 53% solid); [c] Wastes obtained from a pressurized water reactor (PWR) and a boiling water reactor (BWR); [d] No entry indicates compound is below detection level (0.1 ppb); [e] Solid phase of waste from PWR contained no identifiable organics; [f] Identified by GC-MS and FT-IR as molecular weight (MW) 244 lactam; [g] Identified by GC-MS FT-IR as MW 173 lactam; [h] Identified by GC-MS and FT-IR as MW 186 lactam; [i] Four unknown compounds detected: A) unknown, 1.0 ppm; B) unknown, 1.7 ppm; C) MW 247 species, 17.9 ppm; D) MW 318 species, 1.4 ppm

contained most of the hydrophilic organics compared to BWR No.2 (611.1 ppm versus 110.5 ppm for the solid and liquid phases, respectively). This is doubly significant in that the solid of BWR No.1 waste accounted for a significant percentage of the total waste (37% by volume). The opposite was true for the BWR No.2 waste (55.0 ppm versus 16.4 ppm for the liquid and solid, respectively). The same trend was observed for the hydrophobic organic fraction of the BWR wastes. In contrast, the solid phase of the PWR waste did not contain any identifiable organics. The absence of any predictable pattern in the distribution of organics, highlights the general need for thorough source-term characterization of nuclear wastes as a first step in waste treatment scenarios and geochemical investigations.

Complex Concentrate Waste

The organic content of the complex concentrate waste is tabulated in Table III. No hydrophobic organics are reported because none were detected in the waste's hydrophobic organic extract. In contrast, six classes of organics were identified in the hydrophilic organic extract: complexing agents, chelating agents, chelator fragments, carboxylic acids, alkanes and phthalate esters. The concentrations of the organics identified ranged from 0.23 mM to 64.39 mM.

Complexing Agents: Two complexing agents were identified in the complex concentrate waste. Citric acid is by far the most abundant complexing agent at 64.39 mM. Citric acid has been used extensively as a complexing agent, e.g., in the solvent extraction of Sr (4, 5, 13). A second complexing agent, methanetricarboxylic acid, was also identified. Again, this compound is presumably a degradation product derived from citric acid.

Chelating Agents: Three chelating agents were identified in the waste: HEDTA, EDTA and NTA. All three of these compounds are commercially available and have been used extensively in nuclear operations, e.g., to hold Fe and other corrosion products in solution as well as for other process chemistry reasons. As outlined previously, such chelating agents form very strong chelates with a variety of metal ions, particularly heavy metals and actinides (8 - 10).

Chelator Fragments and Organic Diagenesis: The third class of hydrophilic organics identified in the complex concentrate waste are the chelator fragments, presumably derived from the chemical, thermal, and/or radiolytic degradation of the chelating agents. Ten chelator fragments were detected in the waste (Table III). Seven of the chelator fragments have been completely identified. Three have been only partially identified on a molecular weight basis as MW 122, MW 173, and MW 247 species. By far the most abundant chelator

Table III
Organics[a] Identified in Complex Concentrate Waste

	Concentration[b]	
Chelating/Complexing Agents	mM	gC/L
Citric Acid	64.39	4.61
N-(2-Hydroxyethyl)ethylenediaminetriacetic Acid (HEDTA)[c]	37.53	4.53
Ethylenediaminetetraacetic Acid (EDTA)	31.41	3.77
Methanetricarboxylic Acid	17.32	1.45
Nitrilotriacetic Acid (NTA)	7.33	0.53
Chelator Fragments		
Ethylenediaminetriacetic Acid (ED3A)[d]	17.91	1.72
N-(2-Hydroxyethyl)ethylenediamine-N'N'-diacetic Acid (HEDDA)[e]	2.39	0.26
N-(ethylene)ethylenediaminetriacetic Acid (E_2DTA)	2.28	0.23
N-(2-Hydroxyethyl)iminodiacetic Acid (HEIDA)[h]	2.14	0.18
N-(2-Hydroxyethyl)-N'-(methyl)ethylenediamine-N,N'-diacetic Acid (MeHEDD'A)[f]	1.83	0.20
N-(methyl)ethylenediamine-N,N'-diacetic Acid (MeEDD'A)[g]	1.02	0.08
Iminodiacetic Acid (IDA)	187.9	10.92
Molecular Weight (MW) Species[i]		
A: MW 122	0.90	0.04
F: MW 173	0.23	0.02
J: MW 247	0.90	0.08
Carboxylic Acids (e.g. Hexadecanoic Acid)	10.76	1.67
Alkanes $nC_{23} - nC_{35}$	7.77	2.50
Phthalate Esters		
Dibutylphthalate	1.24	0.23
Dioctylphthalate	0.05	0.01
Total Organic Carbon (TOC)	3670	44.00

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[a] Acids identified as methyl ester (BF_3/methanol; [b] Quantitation based on six GC analyses with FID detection; the standard deviations are: citric acid, ± 5.7%; EDTA, ± 7.0%; HEDTA, ± 12.2%; NTA, ± 3.1%; ED3A, ± 2.6%; MeEDD'A, ± 9.1%; Methane Tricarboxylic Acid, HEDDA, E_2DTA, HEIDA, IDA and MeHEDD'A, ± 7.0% each; and MW species, ± 7.0% each. [c-h] Identified by GC-MS and FT-IR as (c) MW 288 lactone; (d) MW 244 lactam; (e) MW 230 dehydrated dimethylester; (f) MW 230 lactone; (g) MW 186 lactam; (h) and MW 173 lactone; [i] MWs assigned to unknown chelator fragments on the basis of electron impact (70 eV) and chemical ionization (CH_4) GC-MS.

liquid chromatography (HPLC) procedures may work for such organics; these alternatives are currently being evaluated.

Polymers are occasionally used in nuclear operations, e.g., flocculating agents such as polyacrylamides and chelating agents such as Dow Chemical's NS-1. Organopolymers could also be formed from the diagenesis of the waste's organic species. Polymeric, nonvolatile organics are not amenable to GC, which requires volatilization into the gas phase for analysis. HPLC, utilizing steric exclusion chromatography, would probably be the procedure of choice. Recent advances in HPLC-MS and supercritical fluid chromatography-MS (SFC-MS) instrumentation may facilitate the identification of the nonvolatile organics, just as GC-MS analysis has made the identification of gas chromatographable organics possible.

CONCLUDING REMARKS

The organic analysis of nuclear wastes poses numerous analytical challenges. Wastes can be highly radioactive, and often exist as multiple phases, i.e., highly ionic aqueous liquids, solids, and suspensions. Some wastes may contain mixtures of diverse organics, including polymeric, polar and nonpolar compounds. In addition, the chemistry of individual organics may be highly complex, e.g., polyfunctional organics. Such factors can render the organic analysis of nuclear wastes very difficult. Fortunately, several advances made in organic analysis over the last few years, e.g., the development of high resolution capillary GC, and computerized GC-MS, facilitate the task immeasurably.

Nuclear wastes may indeed contain complex mixtures of organics, occasionally at relatively high concentrations. Some of the organics, notably the chelating and complexing agents, may interact strongly with radionuclides. Many of the organics are clearly degradation products of source-term organics used widely in the nuclear industry, indicating that organic diagenesis in nuclear wastes can be quite vigorous and extensive. In other words, the organic content of wastes is not static but ever-changing. All of these observations point to the need for continued organic research in the nuclear area. For example, interactions between a waste's organics and radionuclides need to be fully understood before a waste can be properly treated and permanently disposed. Also, understanding the mechanism(s) of organic diagenesis in nuclear wastes may well prove indispensible to optimizing the process parameters of a waste's treatment, e.g., volume reduction.

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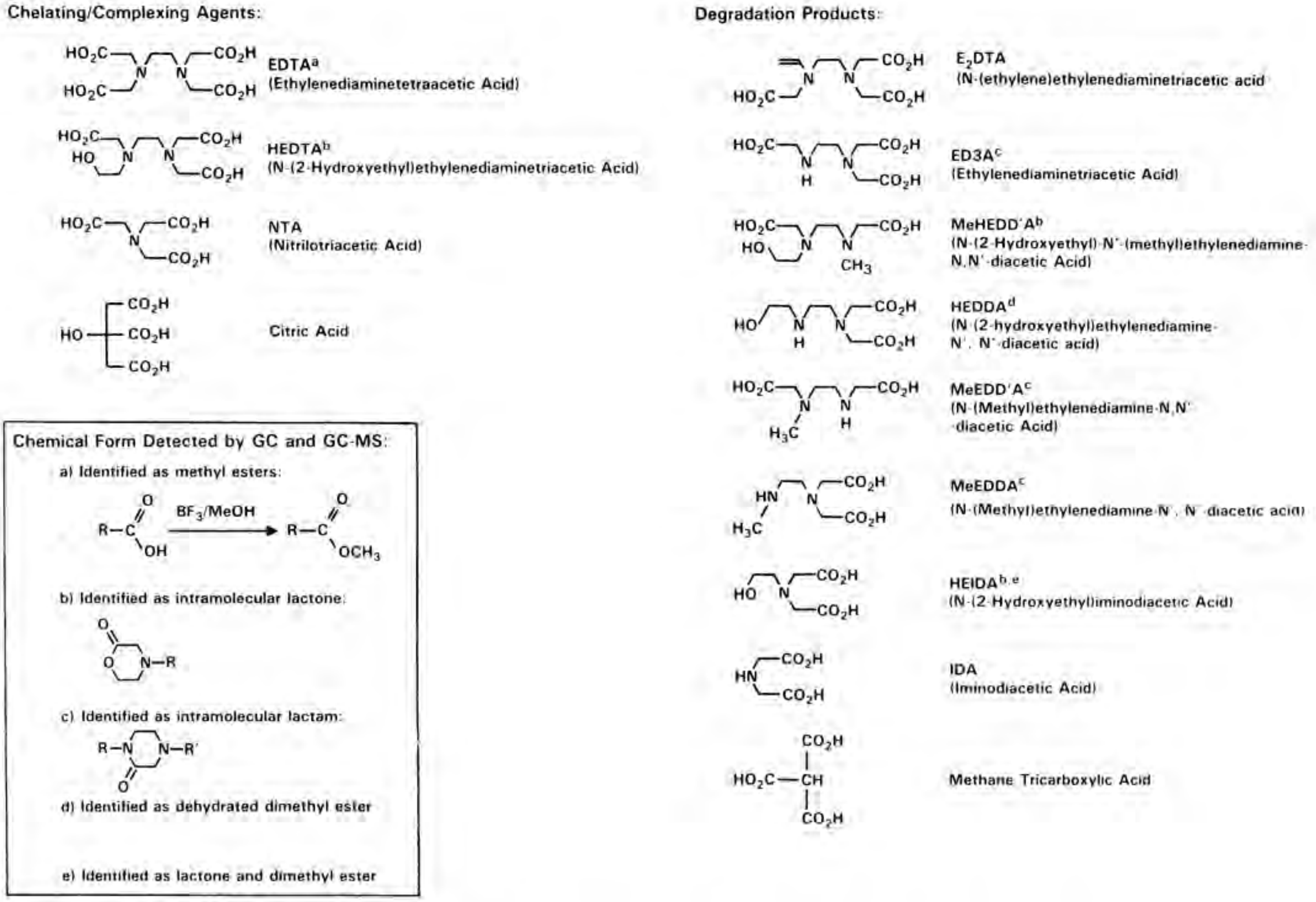

Fig. 1. Chelating/Complexing Agents[a] and Their Degradation Products in Nuclear Wastes.

fragment is IDA at 187.9 mM. The other identified chelator fragments include HEDDA, MeHEDD'A, MeEDD'A, ED3A, E2DTA, and HEIDA, at concentrations ranging from 0.23 mM to 17.91 mM. The structures of these compounds, depicted in Fiq.1, clearly point to varying degrees of degradation of NTA, EDTA, and/or HEDTA. For example there is ample evidence in the literature that HEDTA undergoes chemical and/or biological degradation to form ED3A (2, 10 - 12, 14). As outlined earlier, all of these chelator fragments can chelate/complex metal ions to varying extents.

Chelator fragments account for 74% of the total chelating agent pool in the complex concentrate waste, indicating that organic diagenesis, or degradation, of the waste's organics is substantial. Virtually nothing is known about organic diagenesis in actual wastes. There is ample evidence in the literature, however, that the diagenesis can be highly complex and may occur via chemical, thermal, radiolytic and/or biological mechanisms (2, 15 - 23). These observations demonstrate the need for chemical analyses to determine a waste's actual chemical composition. Some wastes have been stored 20 yr or more, sufficient time for extensive diagenesis to have significantly altered their original organic content. Simply cataloging a waste's chemical content based on its management history may be misleading, if not meaningless.

Other Organics: Three other classes of organics were identified in the complex concentrate waste. A number of monocarboxylic and dicarboxylic acids were identified, ranging in concentration from 0.1 to 2.5 mM. These compounds complex with metal ions but the association is much weaker than that of the metal chelates. A number of alkanes ranging from nC_{23} to nC_{35} were also identified in the waste, accounting for 5.7% of the waste's TOC content. These compounds are undoubtedly derived from oils or solvents. Finally, two phthalate esters were identified, which are commonly used as plasticizers.

Unidentified TOC Content: All of the organics identified to date account for 75.1% of the TOC content of the complex concentrate waste (Table III). This leaves 24.9% of the waste's organic content unknown.

Likely candidates for the missing organic compounds include: 1) low molecular-weight (MW) organic acids; 2) low-MW polar compounds; and 3) high-MW, or polymeric, species. Low-MW organic acids, including oxalic, acetic and glycolic acids are used extensively in the nuclear industry and may be present in the complex concentrate waste. These acids could also be formed from the diagenesis of complexing and chelating agents. Although the analytical procedure developed to methylate and analyze the hydrophilic organic species would make low-MW organic acids chromatographable by GC, their methyl esters would volatilize and be lost in the solvent reduction steps of sample preparation. Also, there may be low-MW, polar organic species that cannot be esterified by methylation and would, therefore, remain unanalyzable by GC. For example, EDTA is known to degrade to methylamines at higher temperatures (>200°C)(3). Other derivatization reactions, e.g. silylation, or high-performance

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