Comparative Efficiencies of Trace Metal Extraction from Municipal Incinerator Ashes

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Five laboratory solvent extraction methods for the determination of leachable trace metals from municipal incinerator fly and bottom ashes are evaluated. The trace elements of interest were cadmium, chromium, copper, manganese and lead. Five different extractants, 0.1 N HCl, 1.0 N ammonium acetate, methyl isobutyl ketone (MIBK), chloroform and hexane were used on each ash to determine comparative extraction efficiencies.

Extraction efficiencies of the five solvents were determined based on total metal concentration, and were found to rank in the following order: 0.1 N HCl > 1.0 N ammonium acetate > MIBK > chloroform > hexane. No one solvent was optimal for obtaining environmentally available values for all five metals. The inorganic solvents, 0.1 N HCl and 1.0 N ammonium acetate, exhibited higher removal of trace metals from ash particles relative to the organic solvents. Manganese concentrations were removed more efficiently by 0.1 N HCl, whereas 1.0 N ammonium acetate was more efficient for removing copper concentrations. Cadmium, Cr, and Pb could effectively be extracted by either of the two inorganic solvents. Concentrations of trace metals extracted from refuse ash appeared to be a function of the elemental boiling point and the species that exist on combustion. However, the classification of elements for refuse ash in this study strayed somewhat from the traditional geochemical classification scheme into which coal ash is placed.

KEY WORDS: Fly ash, municipal incinerator ash, solvent extraction, trace metals, waste-to-energy conversion systems.

INTRODUCTION

The combustion of coal and subsequent emission of fly ash has been reported to be a major source of trace element release to the

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environment.[1-4] Despite the large amount of material released from coal combustion, analyses[4-6] indicate that fossil fuel combustion cannot account for all the trace elements found in urban particulate matter. Because the incineration of municipal refuse as an alternate energy source is increasing, substantial quantities of trace metals on fly ash may be emitted to the atmosphere, thus contributing to the total amount of trace elements found in urban particulate matter.

Examination of fly ash particle surfaces is important because trace metals become sorbed to these surfaces during combustion. Potentially toxic trace elements in coal and refuse (e.g. Se, As, Hg, Pb, Cd, and Zn) become volatilized at the temperatures encountered in the combustion zone and either condense onto smaller particles ($< 1 \mu$m) entrained in the flue gas or are emitted in a vaporized state. The enrichment of certain trace elements on small ash particles has been discussed by several authors.[2,7-12]

This surface predominance of a large fraction of potentially toxic trace elements causes concern for two reasons. First, the occurrence of toxic metals on smaller respirable particles could pose a distinct health hazard since these particle surfaces are directly accessible for extraction by the body fluids following inhalation or ingestion.[13] Second, collected bottom and fly ashes are frequently disposed of by water flushing to temporary ash ponds or sanitary landfills. Disposal of these residues in landfills may result in leaching of trace metals from the particle surfaces and subsequent release into surface and/or subsurface aqueous systems.[14,15]

This paper attempts to identify a laboratory solvent extraction method which indicates the amount of leachable trace metals on municipal incinerator ash potentially available to the environment. Although trace metal extraction methods are numerous and varied, little work has been done to evaluate methods which efficiently extract trace metals from incinerator fly ash for analysis by atomic absorption.

EXPERIMENTAL

Sample collection

Ten municipal incinerator fly and bottom ash samples were collected from six different incinerator sites in The Netherlands: Rotterdam, Alkmaar, Arnhem, Leeuwarden, Amsterdam and Zaanstad. Two wetted bottom ash samples (ZAN_2 and ZAN_3) were collected from a transportation belt below the combustion chamber that continuously carries ash to disposal sites. Eight fly ash samples were collected from electrostatic precipitators in a dry powdered form.

The municipal incinerators in The Netherlands burn only municipal refuse containing no industrial or chemical wastes. Combustibles are not separated from non-combustibles prior to incineration, resulting in a large variation in refuse composition. Electrostatic precipitator emission control devices allow a maximum emission of 100 mg of particles/m^3 of flue gas.

Sample preparation

Samples were air dried, ground, and passed through a 30-mesh sieve. The pH of each sample was determined in slurry form using a Corning Scientific Instruments Model 12 Research pH meter. Five solvent extractions were performed on each of the ten ash samples using 0.1 N HCl, 1.0 N ammonium acetate, MIBK, chloroform and hexane. Five 5.0 g aliquots of each sample were weighed into 50 ml centrifuge tubes and extracted with 20 ml of each solvent for three one-hour intervals using an Eberbach shaker. Following centrifugation after each one-hour extraction, the supernatants were decanted through No. 2 Whatman filter paper to remove any suspended ash particles and brought to a 100 ml volume. Samples extracted in the three organic solvents were concentrated by rotary vaporization to 10 ml. Total metal determinations for cadmium, chromium, copper, manganese and lead were made using an HF-HClO$_4$ acid dissolution.[16] Control blanks without ash were run for each procedure.

Homogeneity within ash samples was tested by examining two different refuse ash samples which were subsampled five times employing a sample splitter to obtain random samples. Replicate extractions performed with 0.1 N HCl for Cd and Mn analyses indicated that variability between samples was less than 8%.

Analysis

Analyses were performed using inductively coupled plasma (ICP) emission spectrophotometry or atomic absorption spectrophotometry (AAS). The standard addition method of analysis was employed for determination of Cd, Cr, Cu, Mn and Pb in the 0.1 N HCl and 1.0 N ammonium acetate extractions, using a model 975 Jarrell-Ash Plasma Atomcomp Inductively Coupled Plasma Emission Spectrophotometer. Determination of Cd, Cr, Cu, Mn and Pb in the organic solvent extractions and in the total metal solutions was made by use of a Perkin Elmer Model 303 Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

The five solvents used for trace metal extraction serve as the basis for the extraction efficiency data. The HF-HClO$_4$ acid dissolution provided solutions for the determination of the total metal content in each sample. From these data the portion of extractable metals (for each of the solvent extraction procedures) was expressed as a percentage of the total metals present (Figures 1–5).

The analyses of trace metals in refuse ash illustrate that considerable variation exists in the percent of metals removed utilizing different extraction procedures. It is apparent from these data that it is difficult to make comparisons of refuse ash metal concentrations published in the literature unless extraction solutions are similar and extraction procedures are described in detail. Although our choice of extraction solutions in this study might be criticized, our purpose was to choose solvents that remove metals indicative of environmentally available metals, i.e. metals found predominantly on the particle surface.

The strong acid digestion (HF-HClO$_4$) caused complete dissolution of the ash particles, releasing trace metals held in the matrix material and providing total metal concentrations. However, conditions for complete
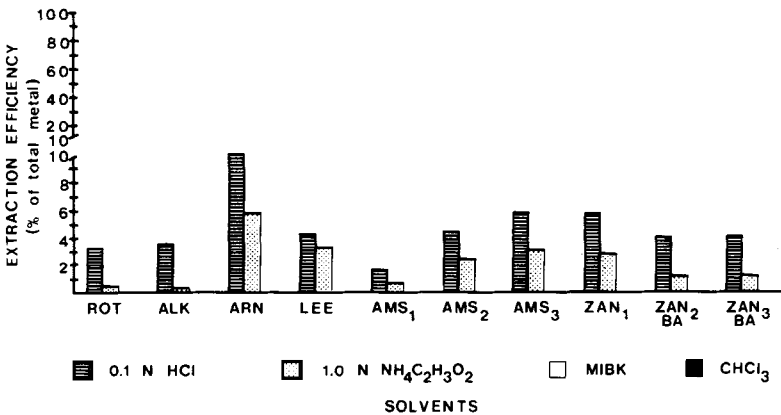
FIGURE 1   Manganese solvent extraction efficiencies for municipal incinerator ash. Legend for sample sites is given below.

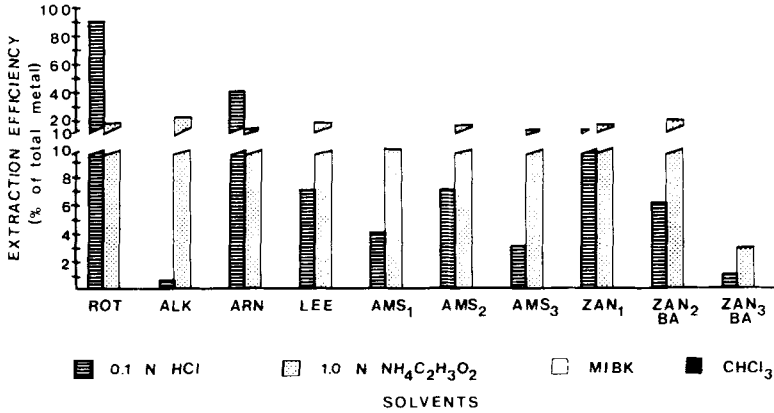|	
ROT = Rotterdam	AMS$_3$ = Amsterdam (8/14/78)
ALK = Alkmaar	ZAN$_1$ = Zaanstad
ARN = Arnhem	ZAN$_2$ = Zaanstad (4/14/78)
LEE = Leeuwarden	ZAN$_3$ = Zaanstad (9/27/78)
AMS$_1$ = Amsterdam (9/12/78)	BA = Bottom ash
AMS$_2$ = Amsterdam (9/28/78)	

FIGURE 2 Copper solvent extraction efficiencies for municipal incinerator ash.
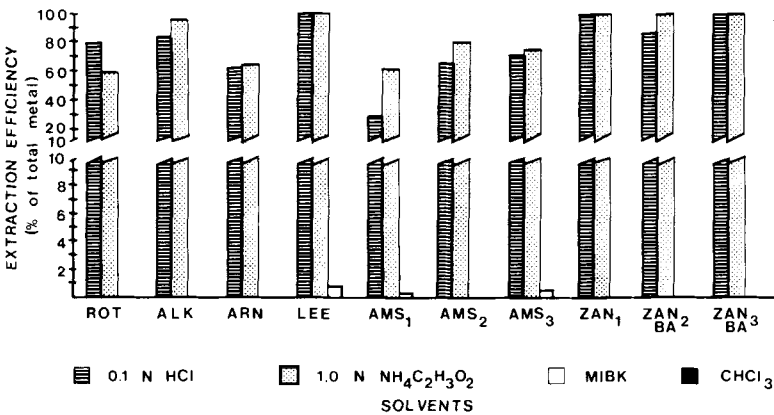
FIGURE 3 Cadmium solvent extraction efficiencies for municipal incinerator ash.

dissolution of fly ash particles seldom occur in nature, therefore, the total metal concentrations indicated by this digestion procedure are not representative of concentrations that are a major environmental concern. The elements leached by the following solvent extraction procedures are of greater concern.

The extraction solutions are classified into two categories, inorganic (acid and ion displacive) and organic. The results from extractions using the two inorganic solvents, 0.1 N HCl and 1.0 N ammonium acetate, and the three organic solvents, MIBK, chloroform, and hexane, showed that
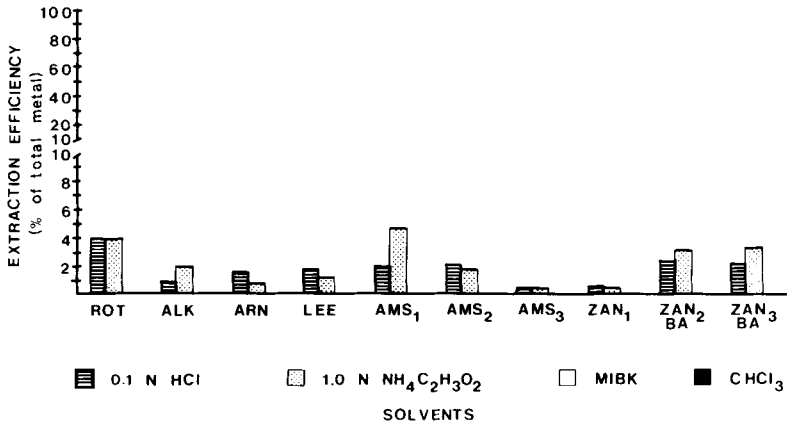
FIGURE 4   Chromium solvent extraction efficiencies for municipal incinerator ash.
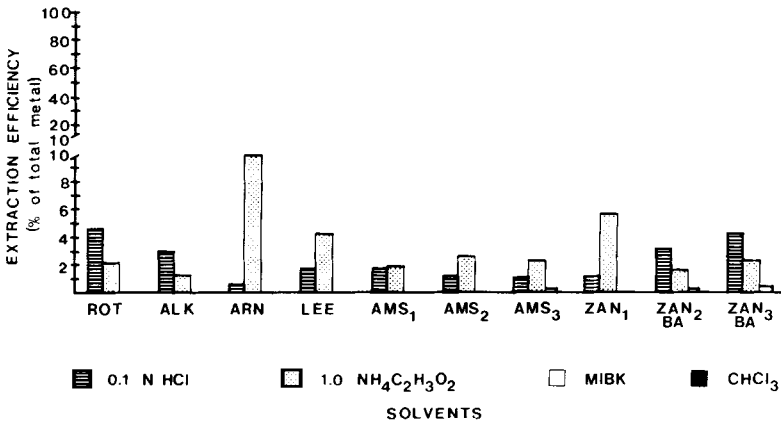
FIGURE 5   Lead solvent extraction efficiencies for municipal incinerator ash.

the inorganic solvents exhibited higher removal of trace metals from ash particles. It is obvious from the data that no one of the extraction solutions is optimal for obtaining environmentally leachable values for all five metals. Figure 1 indicates that 0.1 N HCl is more efficient for removing concentrations of manganese, whereas 1.0 N ammonium acetate extractions produced the higher percentage of copper (Figure 2). Cadmium, Cr, and Pb could effectively be extracted by either of the two inorganic solvents (Figures 3, 4, and 5).

Acid solutions, e.g. 0.1 N HCl, cause dissolution of soluble condensed compounds on the fly ash particle surface, such as the oxides of

manganese and iron. Preliminary batch extractions performed for two metals from refuse ash with dH_2O, 0.1 N HCl, 1.0 N HCl, and 6.0 N HCl indicated that increasing amounts of Cd and Mn were removed with increasing acidity (Figure 6). Cadmium and manganese were chosen for analysis because of their different presumed mechanisms of ash deposition during combustion. Cadmium exhibits surface predominance whereas manganese exhibits matrix predominance.

These data support a study by Green and Manahan[17] in which coal fly ash particles were found to dissolve in discrete steps with increasing solvent acidity (utilizing dH_2O, 1.0 N HCl, 6.0 HNO_3, and aqua regia-HF dissolution), thereby releasing increasing trace element concentrations. An increase in extractability of Cd, Cr and Cu from coal fly ash was also observed by Dreesen et al.[18] as acidity of the solvent increased. These
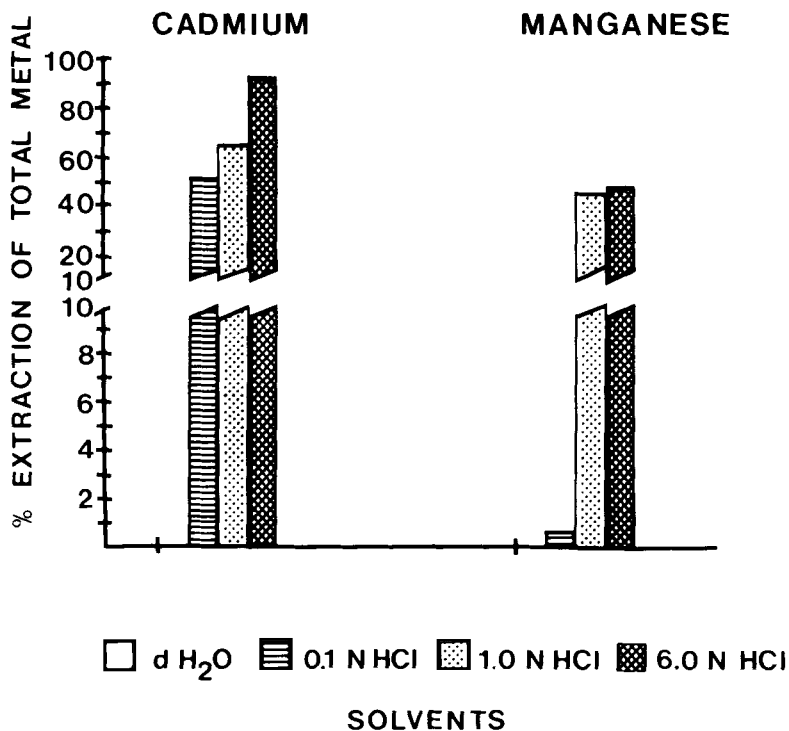

FIGURE 6   Percent of total cadmium and manganese extracted by distilled water and increasing concentrations of hydrochloric acid.

authors suggest that surface predominance was an important factor influencing the release of trace elements from ash.

Ion displacive solutions such as ammonium acetate, cause previously adsorbed cations to be replaced by the mass action of new ions supplied in abundance by a solution.[19] A study utilizing selective extraction procedures to approximate the association of metal species with different solid fractions of coal ash, indicated that the ammonium acetate extraction solutions contained trace metals which were replaceable by ammonium ions.[20] Ion displacive solutions are often used for the determination of cation exchange capacity (CEC) in soils.[21] However, low CEC values measured on the refuse ash samples (0.3–8.5 meq/100 g ash) indicate that ion displacive activity is probably not the major mechanism by which 1.0 N ammonium acetate removed trace metals from municipal incinerator ash particles. Instead, solubilization by 1.0 N ammonium acetate of the surface deposited metals most likely occurred. Therefore, the majority of metals on these refuse ashes probably do not occur as adsorbed cations on the ash particle surfaces, but as a coating of metal oxides. Davison et al[8] and Linton et al[22] also suggested that during combustion, metals become deposited on fly ash particles as metal oxides by means of the volatilization-condensation reaction mechanism.

The three organic solvents were used to investigate the possible presence of organometallics in refuse ash. Organic molecules have been found in refuse ash[23] and it therefore was postulated that organometallics might be present.

MIBK is a favored organic solvent for extraction of metal chelates. In atomic absorption analysis, MIBK also gives good enhancement to metal absorbances because its low viscosity results in a faster aspiration rate during analysis than water.[24–26] In this investigation MIBK was used directly as the extraction solvent to determine the potential availability to the environment of organometallics occurring on the particle. However, very small percentages (0.3–1.0%) of Cd and Pb were extracted by MIBK as shown in Figures 3 and 5, respectively.

Metals removed by chloroform were at non-detectable levels with the exception of trace amounts of Cd, Cu, and Pb. Chloroform is not a good extraction solvent due to its low polarity.

Hexane, due to its non-polarity, exhibited the poorest efficiency of trace metal extraction. No metal concentrations could be detected from any of the ten ashes extracted by hexane. Therefore, hexane as an extraction solvent does not appear on Figures 1–5.

Low concentrations of metals extracted by the organic solvents possibly indicate very low or no surface deposited organometallic compounds on the ash.

Classification of elements in refuse ash

Based on the results of solvent extractions performed on refuse ashes, the inorganic solvents removed concentrations of metals more representative of the amounts potentially mobile in an ash disposal site. The metals most likely to be leached are those that occur principally as surface deposited metals. The primary factor that determines whether a metal will occur in the matrix or will be surface deposited is its boiling point.[8] Elements with low boiling points typically exhibit high extractability whereas elements with high boiling points show lower extractability. A "volatilization–condensation" mechanism occurs when trace metals such as cadmium and lead volatilize in the high temperature combustion zone at 1500–1600°C, and then condense at lower temperatures onto the surfaces of less volatile metals such as manganese, silicon, and aluminum.[1,8,13] The boiling points of the metals analyzed and their compounds are given in Table I.

TABLE I

Boiling points of possible inorganic species evolved during combustion[8]

Species boiling or subliming, < 1550°C	Species boiling or subliming, > 1550°C
Cd, CdO, CdS	Cr, Cr_2O_3
$Cr(CO)_6$, $CrCl_3$, CrS	Cu, CuO
$PbCl_2$, PbO, PbS	Mn, MnO, MnO_2
	Pb

In support of the volatilization–condensation mechanism, the elements that occur in coal ashes have been divided into four classes as proposed by Klein et al:[3]

Class I. Al, Ba, Be, Ca, Co, Fe, K, Mg, Mn, Si, Sr, Ti;
Class II. As, Cd, Cu, Ga, Pb, Sb, Zn, Se;
Class III. Hg, Cl, and Br remain essentially in the gas phase;
Class IV. Unclassified elements exhibiting properties of either Class I or Class II—Cr, Cs, Ni, U, V.

In an attempt to place metals derived from refuse ashes in the geochemical classification by Goldschmidt[27] and Mason[28] or the classification scheme for coal ashes proposed by Klein et al[3] modifications were made to rationalize the classes of behavior for the refuse ashes studied.

The Class III elements Cl, Hg, and Br are highly volatile and are present as gases at all times during the combustion process. No analyses for Class III metals were performed in this study.

Class I elements, which include manganese, have boiling points above the oven temperatures and are not volatilized in the combustion zone. Instead they form a melt of uniform composition that becomes the matrix. Class I elements remain in the condensed state and exhibit minimal surface deposition. In this study the refuse ashes show the same trend. Only a small percentage of the total Mn (0.5–10%) was extracted from the surface of the ash particles by any of the solvents tested (Figure 1). Table I shows the boiling points for Mn, MnO, and MnO_2, common environmental fly ash forms, to be above 1550°C.

Class II elements are volatilized during combustion and have little opportunity to become incorporated in the bottom ash. These elements, including Cd, Cu, and Pb, condense or become adsorbed on the fly ash particle surface as the flue gas cools. Figure 3 indicates that the average amount of Cd extracted from the refuse ashes (80%) was predominantly surface deposited. The boiling points of the cadmium species evolved during combustion (Cd, CdO, and CdS) are below the combustion temperatures. However, because the different compounds of Pb and Cu evolved during combustion exist at temperatures above and below 1550°C (Table I), their surface predominance and subsequent high extractability are not as apparent. The boiling points of $PbCl_2$, PbO, and PbS are below 1550°C, but the low percentages of lead extracted (0.5–10%) from the ash surface (Figure 5) indicate that most of the lead possibly occurs in the ash as lead metal (Pb°). The lead extraction from refuse ashes resembles characteristics of the Class I elements. Very high concentrations of lead were found in the total metal solutions, suggesting that the acid dissolution released large amounts of lead from the matrix.

Copper and CuO have boiling points above the combustion temperature. Figure 2 shows that 90% of the total Cu was removed from sample ROT by 0.1 N HCl, while most other sample extractions showed 1–20% removal for Cu. The coal classification scheme puts copper in Class II, but for refuse ashes copper appears to fall into Class IV, exhibiting properties intermediate between Class I and Class II.

Chromium has been classified as intermediate between Class I and Class II for coal ashes but appears to fall into Class I for refuse ashes. Low percentages of chromium (0.5–5%) were extracted from the ash as shown in Figure 4, although the boiling points of $Cr(CO)_6$, $CrCl_3$, and CrS are below 1550°C. The chromium in the ash is probably present as metallic chromium (Cr°) or Cr_2O_3, both species having boiling points above combustion temperatures.

SUMMARY AND CONCLUSIONS

The trend toward utilizing refuse as an energy source either as a supplement to coal or oil in power plants or steam generators, or as a source of methane for the natural gas industry, suggests that methods to characterize environmentally available metals from these refuse ashes should be evaluated. The extraction methods considered in this paper indicate that, of the five solvents examined, the inorganic solvents, 0.1 N HCl and 1.0 N ammonium acetate, removed elements associated with the particle surface. The 0.1 N HCl probably extracts metals most representative of acid leachable metals since these are believed to be present as condensed surface oxide coatings rather than adsorbed cations. In addition, dissolution of the refuse ashes was shown to be a function of solution acidity. Ash particles were found to dissolve in steps with increasing acidity providing an indication of metals that exhibit surface predominance. Metals removed in this manner can be leached out whenever the pH of the water in contact with the ash is lowered by biological oxidation or introduction of an acidic medium. Finally, the three organic solvents, MIBK, chloroform and hexane, extracted only trace amounts of organometallic concentrations.

For the refuse ashes studied, cadmium and manganese exhibited clear elemental partitioning whereby cadmium was preferentially coated on the particle surface and manganese was found as a matric component. Separating the remaining metals analyzed, Cr, Pb, and Cu, into behavioral classes was not as clearly defined. Although most Class I elements are relatively high boiling and most Class II elements are low boiling, there are different species of the same element, e.g. $CrCl_3$ with a boiling point $< 1550°C$ and Cr_2O_3 with a boiling point $> 1550°C$, in both classes making elemental boiling point only one of many factors determining elemental partitioning during combustion of refuse. It is probable that the state of the element in the refuse prior to combustion will also influence the behavior upon combustion. Based on the boiling points of the various metal species and their respective percentage removal by the organic solvents, the following classification scheme was developed:

Class I.   Includes Mn, Cr, Pb; exhibit low volatility; low percentages of surface extraction observed.

Class II. Includes Cd; highly volatile; high surface extraction observed.

Class III. None analyzed.

Class IV. Includes Cu; exhibits properties intermediate between Class I and Class II elements.

Acknowledgements

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