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**Leaching Characteristics of Heavy Metals
from NYC Biosolids**

By

Tianqing Liu

A dissertation submitted to the Graduate Faculty in
Chemistry in partial fulfillment of the requirements
for the degree of Doctor of Philosophy,
The City University of New York.

1996

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requirement for the degree of Doctor of Philosophy.

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Abstract
Leaching Characteristics of Heavy Metals
from NYC Biosolids
by
Tianqing Liu

Advisor: Professor David C. Locke

A unique leaching column apparatus was constructed to study the leaching of heavy metals from sewage sludge products applied to different soil types. Two sewage sludge products from the sewage treatment plants of New York City, composted and thermally dried sludges, which are intended for agricultural and land applications, and two types of soil, sandy and urban organic-rich soils were studied in this research. Synthetic rain water was applied to the leaching columns and the concentrations of 11 heavy metals in the effluent from the columns were monitored continuously. A strongly acidic pH 1.5 leaching solution causes extensive leaching of heavy metals, but no significant leaching was observed between pH 4.0 and 4.5, the common pH values of NYC rain water in summer and winter. Soils with higher organic contents and cation exchange capacity retain heavy metals leached from sewage sludge more strongly and hence can prevent ground water from being contaminated by heavy metals. The mobility of heavy metals from thermally dried sludge is relatively low compared with composted sludge, suggesting the good quality of the thermally dried sludge

product. The characteristics of individual heavy metal elements bound to inorganic and organic moieties in sludge and soil were addressed. Safe usage of different sludge products applied to various soil types was predicted based on the results of this research.

The analytical techniques, flame atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), and inductively coupled plasma- atomic emission spectrometry (ICP-AES) were optimized to analyze the leachate samples. Matrix modifiers in GFAAS was successfully used for analysis of volatile metals in the leachates at the highest sensitivity level. ICP-AES is one of the most reliable analytical techniques, and is applicable to many different types of samples. However, when ICP-AES is applied to environmental samples such as leachates from the sewage sludge products, in which a matrix-matched calibration is extremely difficult, special care must be taken to optimize instrumental sensitivity and detection limits for trace analysis. Signal-to-noise ratio and detection precision were much improved by the use of increased integration time, internal standardization, and background correction and interelement correction techniques.

DEDICATED

TO

MY WIFE XIAOLEI GAN

AND

MY DAUGHTER KELLY

献 给

我们亲爱的父母

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List of Abbreviations

AAS	Flame atomic absorption spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
ICP-AES	Inductively coupled plasma- atomic emission spectrometry
RSD	Relative standard deviation
std	standard
Ave	Average
Dev	Deviation
USN	Ultrasonic nebulizer
S/N	Signal to noise ratio
B.E.C.	Background equivalent concentration
DL	Detection limit
AIDL	Absolute instrumental detection limit
LI	Long Island, New York
LR	Lime requirement
BpH	Buffer pH
CEC	Cation exchange capacity
DWS	Dewatered Sludge
CPS	Composted Sludge
TDS	Thermally dried sludge
S15	Leachate from LI sandy soil column using pH 1.5 solution
S40	Leachate from LI sandy soil column using pH 4.0 solution
S45	Leachate from LI sandy soil column using pH 4.5 solution
S56	Leachate from LI sandy soil column using pH 5.6 solution

R40	Leachate from Brooklyn urban soil column using pH 4.0 solution
C40	Leachate from neat composted sludge column using pH 4.0 solution
D40	Leachate from neat dewatered sludge column using pH 4.0 solution
T40	Leachate from neat thermally dried sludge column using pH 4.0 solution
CS40	Leachate from composted sludge treated LI sandy soil column using pH 4.0 solution
CS45	Leachate from composted sludge treated LI sandy soil column using pH 4.5 solution
CR40	Leachate from composted sludge treated Brooklyn urban soil column using pH 4.0 solution
TS40	Leachate from thermally dried sludge treated LI sandy soil column using pH 4.0 solution
TS45	Leachate from thermally dried sludge treated LI sandy soil column using pH 4.5 solution
TR40	Leachate from thermally dried sludge treated Brooklyn urban soil column using pH 4.0 solution

Chapter 1 Introduction

1.1 Background of sewage sludge treatment in NYC

Since 1938, New York City , along with other towns and cities in the region, has been dumping its sewage sludge at a designated ocean location (Figure 1.1). This site was designated the acceptable alternative to sewage discharge into upper New York Bay [1]. Permits regulating use of the 12 mile site were issued pursuant to the Marine Protection Research and Sanctuaries Act of 1972 as amended in 1977, 1981, and 1988. On March 17, 1986, a new site, the 106 Mile Deepwater Municipal Sludge Dump Site (DMSDS) was designated to replace the 12 Mile Site by the U. S. Environmental Protection Agency (EPA). Permits for disposal at DMSDS were interim and were scheduled to expire on August 14, 1989. However, the City was granted a special permit to continue to use the site.

During this same period, the Ocean Dumping Ban Act (ODBA) required that the City enter into a compliance agreement with the EPA to consider alternatives to ocean disposal as a condition for obtaining such a special permit, and to develop and implement a land-based sludge management program. The proposed plan included a preferred operational plan with six processing facilities throughout NYC to compost, chemically stabilize, and thermally dry sludge after dewatering for a land-based, beneficial use of the city's sludge beginning 1998 [2].

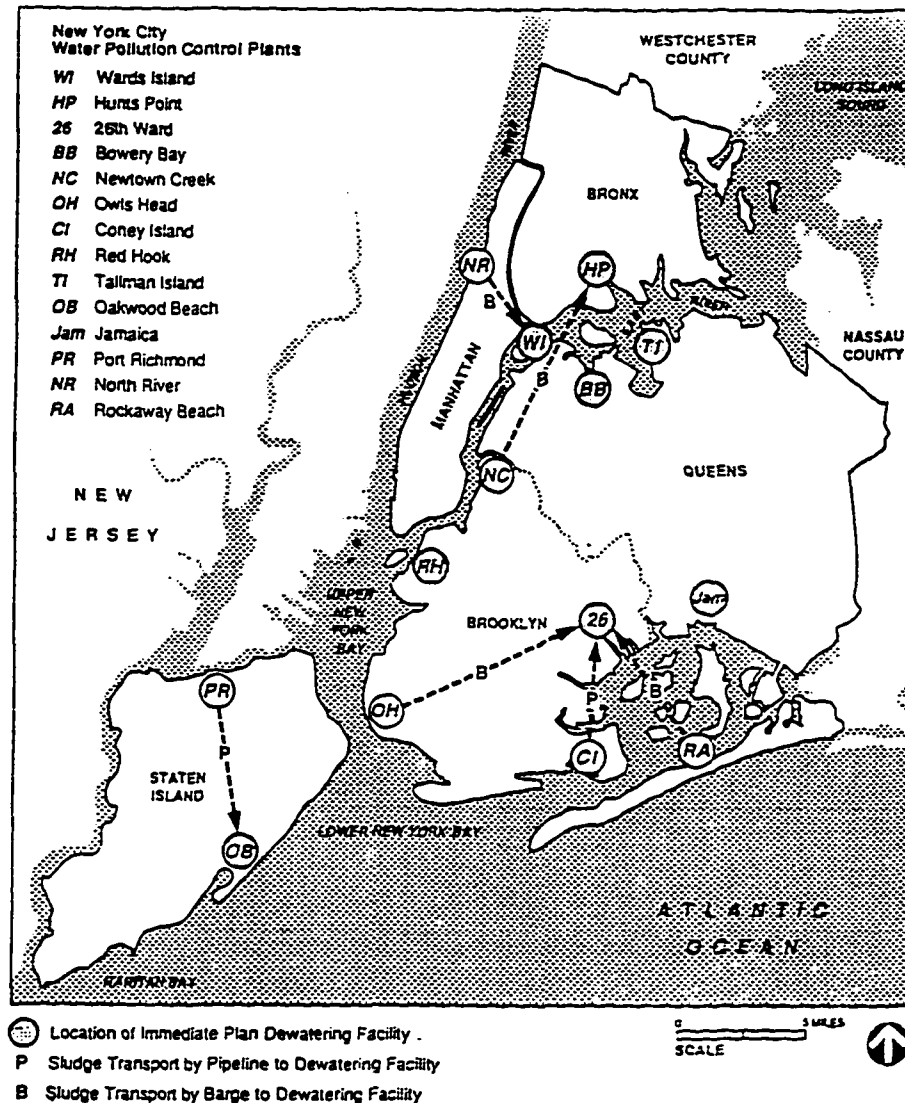


Figure 1.1 New York City Water Pollution Control Plants (from Reference 4)

The potential uses include filler material in agricultural grade fertilizers, ingredient in specialty fertilizers, and ingredient in landscaping products. Therefore to thoroughly evaluate the sewage sludge products before initiating large scale commercial marketing is imperative.

1.2 Land application of sewage sludge and its problems

Because sewage sludge disposal practices (e.g., ocean dumping and landfilling) are becoming less available and more costly, and because of the increasing desire to beneficially reuse waste residuals whenever possible, land application is increasingly chosen as a sewage sludge use or disposal practice. It involves taking advantage of the fertilizing and soil conditioning properties of sewage sludge by spreading the sewage sludge on the soil surface, incorporating or injecting the sewage sludge into soil, or spraying the sewage sludge so that the nutrients (e.g., nitrogen, phosphorus) and organic matter in sewage sludge can be beneficially used to grow crops or other vegetation.

Over the years, land application has increasingly been managed to protect human health and the environment from various potentially harmful constituents typically found in sewage sludge [3,4]. Management of the land application of sewage sludge has included regulatory measures; voluntary and mandatory pretreatment of wastewater and/or sludge by industry to improve quality (e.g., lower

pollutant levels); and use of good management practices at land application sites.

One of the main problems associated with the safe commercial utilization of sludge products is that they contain heavy metals at levels potentially toxic to plants, animals and humans. The "term heavy metal" usually refers to metals with densities greater than 5.0 and includes such elements as Cd, Cu, Pb, Ni and Zn. Since sanitary and storm sewers are generally combined in NYC [5], even with effective industrial pretreatment programs, these heavy metals can enter wastewater through household effluents as well as through storm sewers from street runoff. If these sludges are processed and applied to land, it is important to determine whether the toxic components can become mobilized as the applied sludge ages and is acted upon by soil biota and by precipitation. Solubilization of heavy metals allows them to be leached by rainwater into the subsoil and potentially into groundwater, and makes them available to plants and to soil microorganisms.

1.3 Previous studies of heavy metal characteristics from sewage sludge application in environment

Several studies have been published showing data on the metal concentrations found in sewage sludges [6-14]; it is readily apparent from the available data that a typical sewage sludge does not exist from the standpoint of metal content. The chemical species of metals present

in sewage sludge applied to soils undoubtedly influences subsequent availability of these metals to plants. There are a number of general chemical forms of metals in soils and sewage sludges that differ in their mobility and plant availability [15]. These include:

1. Water-soluble metals
 - a. Soluble as free ions, e.g., Zn^{2+}
 - b. Soluble as inorganic complexes
 - c. Soluble as organic complexes
2. Exchangeable metals
3. Metals precipitated as inorganic compounds
4. Metals complexed with high molecular weight humic materials
5. Metals adsorbed on or occluded to precipitated hydrous oxides
6. Metals precipitated as insoluble sulfides
7. Metals bound within the crystalline lattice structure of primary minerals.

Water-soluble metals are of course the most mobile and plant-available. Exchangeable metals are those bound to soil surfaces by a cation exchange process. Metals in this form are considered weakly bound and may be displaced relatively easily to the water-soluble form. Together, metals in the soluble and exchangeable forms are considered readily mobilized.

Metals precipitated as inorganic compounds generally include metal oxides, hydroxides, and carbonates. The stability of these inorganic metal compounds is controlled primarily by the system pH. At

near-neutral to somewhat alkaline pH levels, metals tend to be effectively immobilized. If, however, pH becomes moderately to strongly acid, these metals may be released to more mobile forms.

It is well established that oxides of Fe and perhaps Mn and Al effectively adsorb or occlude most trace and toxic metal cations [16,17]. These hydrous oxides of Fe are common in upland soils and sludge applied upland. Giblin et al.[18] has shown iron oxides and iron hydroxides are important in retaining metals in a surface sediment of a salt marsh receiving trace and toxic metals from sewage sludge applications used as a fertilizer.

Techniques used to characterize heavy metals in soils and sewage sludge can be categorized into two groups, selective extraction methods and instrumental surface analyses. Extraction methods have been applied extensively by soil scientists for metal analysis, leaching of metals from soil and sludge, nutrient availability for plants, and studies of fate and mobility of the metals in the soil environment [19-24]. These methods were developed on the assumption that it is possible to separate heavy metals present in soils and sludges into different geochemical phases. Multiple extraction steps with chemical reagents of various strengths, reaction times, temperature, and pH conditions have been proposed and used. Periodically, extensive reviews of extraction methods have appeared in the literature [25-28]

Apart from errors arising due to the lack of extractant selectivity, metal re-adsorption, and sample handling, the inability to validate the

procedure itself appears to be a major drawback of sequential extraction techniques [29]. Despite these problems, it has been argued that sequential extraction procedures provide a pragmatic approach for discerning heavy metal speciation in sewage treated soils [30].

The majority of the reported procedures found in the literature using selective extraction for metal speciation in soil and sludge are variants of the approach proposed by Tessier et al. [31]. The method of Tessier et al. operationally groups heavy metals sludge treated soils into five fractions: exchangeable, carbonate, Fe-Mn oxide, organic, and residual fractions. Different extractions and operating conditions such as pH, time, and temperature are used to remove metals held in the various fractions as selectively as possible.

Another approach to the elucidation of heavy metal distribution in soil components involves the use of instrumental surface analytical techniques such as Auger electron spectroscopy (AES), SEM, energy dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS or ESCA), and secondary ion-mass spectroscopy (SIMS). Although these techniques have been used to some extent for the determination of the speciation, availability, and surface association of elements present on geological samples [32-39], their applications for sludge treated soil has been limited [28].

Unfortunately, to date, little work has been done to develop a methodology that can be used to determine appropriate extractants, operating conditions, and expected performance for sewage sludge, soil

and sludge treated soil systems. Typical soil determinations such as soil pH, cation exchange capacity (CEC), organic and moisture content, particle-size distribution, soil classification, and total elemental analysis do not provide sufficient information to answer questions concerning heavy metal distribution, and their mobility from sewage sludge application in real cases [40].

1.4 Objectives of this research

The objectives of this research were to: (1) characterize the mobility of heavy metals from two sewage sludge products applied to two types of soil using a dynamic leaching apparatus with simulated rain water; (2) determine the effect of pH on leachability of heavy metals; (3) relate the leachability of heavy metals to the type of sewage sludge treatment product; (4) evaluate the usage of sludge products following the government guidelines; (5) relate the retention of heavy metals to the characteristics of soil; and (6) determine the effect of lime-treated soil on the pH buffer capacity and the heavy metal leachability.

The other goals of this research were: 1) to investigate the ability of different instrumental techniques to analyze the complicated environmental samples; 2) to optimize the conditions for flame atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), and inductively coupled plasma atomic emission spectrometry (ICP-AES); 3) to establish a ICP-AES analytical

procedure to compare with AAS and GFAAS in terms of analysis rate, detection limit and precision, to determine if it could substitute for AAS as a routine analytical technique, and GFAAS as a more sensitive analytical technique for environmental samples.

Chapter 2 Elemental Analysis by Atomic Absorption Spectrometry

Because of the complex nature of environmental samples, special care must be taken in sample preparation, preservation, and instrumental optimization. The initial work in this research required analytical methods be developed or modified to analyze sludge, soil and leachate for heavy metals. At the beginning of this project, an atomic absorption spectrometer with flame or furnace AAS as atomization sources was used for elemental analysis. An ICP-AES instrument was used subsequently. This provided a good opportunity to do a comparative study of heavy metal determination by AAS and by ICP-AES in sludge and soil leaching solutions.

2.1 Elemental Analysis by Flame AAS

Until recently, flame atomic absorption spectroscopy was the most widely used of all atomic spectral methods because of its simplicity, effectiveness, and relatively low cost [41]. This position of preeminence is now being challenged, however, by inductively coupled plasma spectroscopy, an emission method described in the following chapter. Even though it is of lower sensitivity than furnace AAS and slower in analytical performance than ICP for environmental sample analysis, flame AAS provides a rapid and simple analytical method for elements which are present at ppm levels in leachates (See Table 2.1).

Table 2.1. Sensitivity (ppb) for Selected Elements

Element	Flame AAS *	Furnace AAS		ICP-AES	
		Ref. 43	This work	Ref. 44	This work
As	100	1.2		3	4
Cd	5	0.5	0.2	0.3	0.2
Cr	10	1.5	1.2	0.3	0.9
Cu	10	2.0	0.9	0.3	0.3
Fe	3	1.0	0.7	0.2	0.3
Mn	15	2.0	1	0.2	0.2
Mo	30	15.0		0.2	1
Ni	40	11.0	1.5	1	0.8
Pb	10	5.0	1.8	3	2
Se	70	10.0		1	1
Zn	8	1.0	0.8	0.3	0.4

AAS = atomic absorption spectroscopy, AES = atomic emission spectroscopy, ICP = inductively coupled plasma.

2.2 Instrumental Conditions for Flame AAS

A Perkin Elmer Model 3030B AAS with deuterium beam continuous background correction was used for Fe, Mn, and Zn determination in the leachates at the beginning of the experiments. The hollow-cathode lamp lines used were 248.3 nm for Fe, 279.5 nm for Mn, and 213.9 nm for Zn, with an air-acetylene (C_2H_2 4.0 L/min.) flame and 10 cm burner head. The Model 3030b software version 02.01 was used as a control and calculation program.

The working standard solutions were prepared from 1000 ppm standard solutions manufactured by CPI, Santa Rosa, CA. All dilutions were prepared using glass-distilled water that was then put through a Millipore Milli-Q System, which provides anion- and cation-exchange, activated charcoal filtration, and filtration through a 0.45 micron filter. In order to be consistent with sample preparation, the working standard solutions were prepared in 0.2 % nitric acid diluted from ultrapure concentrate nitric acid (J. T. Baker Chemical Company, Phillipsburg, New Jersey). Where necessary, samples were diluted so that their absorbance values fell on the linear part of the respective calibration curves. Blank and standards were analyzed after about every fifth sample to correct for instrumental drift. The standard concentrations are listed in Table 2.2.

Table 2.2 Concentration of Standards (ppm) for Flame AAS and
Operating Conditions

	Std 1	Std 2	Std 3	Std 4	Wavelength nm	Slit setting nm
Fe	2.00	4.00	6.00	10.0	248.3	0.2
Mn	0.50	1.0	2.00	5.00	279.5	0.2
Zn	0.20	0.50	1.00	2.00	213.9	0.7

2.3 Standard Addition vs. External Standard Calibration Methods in Flame AAS

Ideally, calibration standards should approximate the composition of the samples to be analyzed not only with respect to the analyte concentration but also with regard to the concentrations of the other species in the sample matrix in order to minimize the effects of the various components of the sample on the measured absorbance. Unfortunately, when the complex leachates from soils and sludge are analyzed, preparation of standards that match the samples is impossible or extremely difficult. However, the standard addition method should be helpful in counteracting matrix effects.

In this experiment, a group of representative samples was selected to evaluate the deviations between the standard addition method and external standard calibration method. For external standard calibration method, the working standard solutions in Table 2.2 were calibrated first as in Figure 2.1, absorbance of leachate samples were measured, and concentrations were directly read through the calibration curves (Figure 2.1 for Fe). In the standard addition method, the calibration is performed by mixing each leachate solution with several equal aliquots of working standard solution. The calibration set therefore consists of a number of spiked samples plus the unspiked original sample to which an equal volume of 0.2% HNO_3 was added, so that all solutions have an almost identical matrix. A typical standard addition

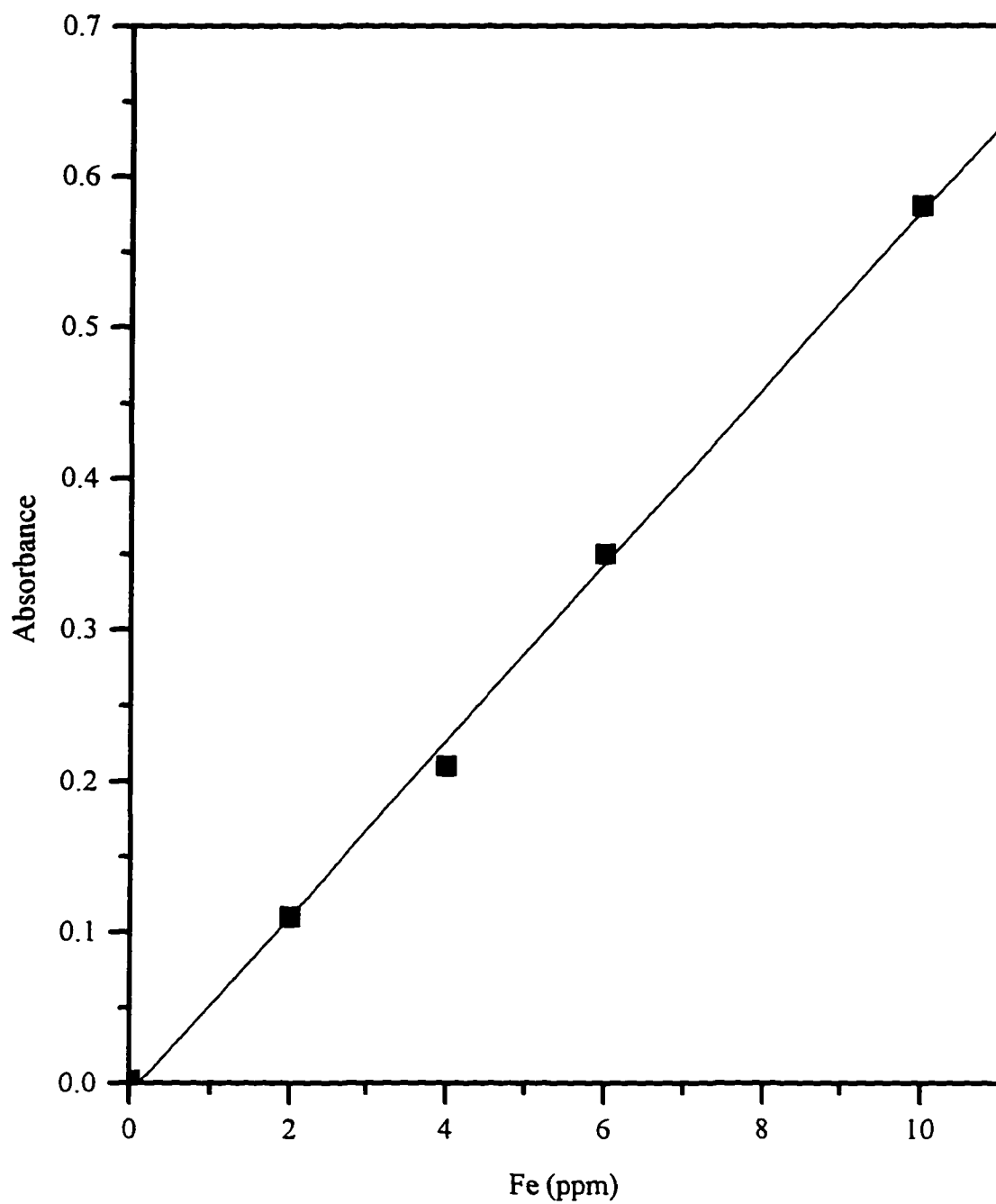


Figure 2.1 Standard Calibration Curve for Fe

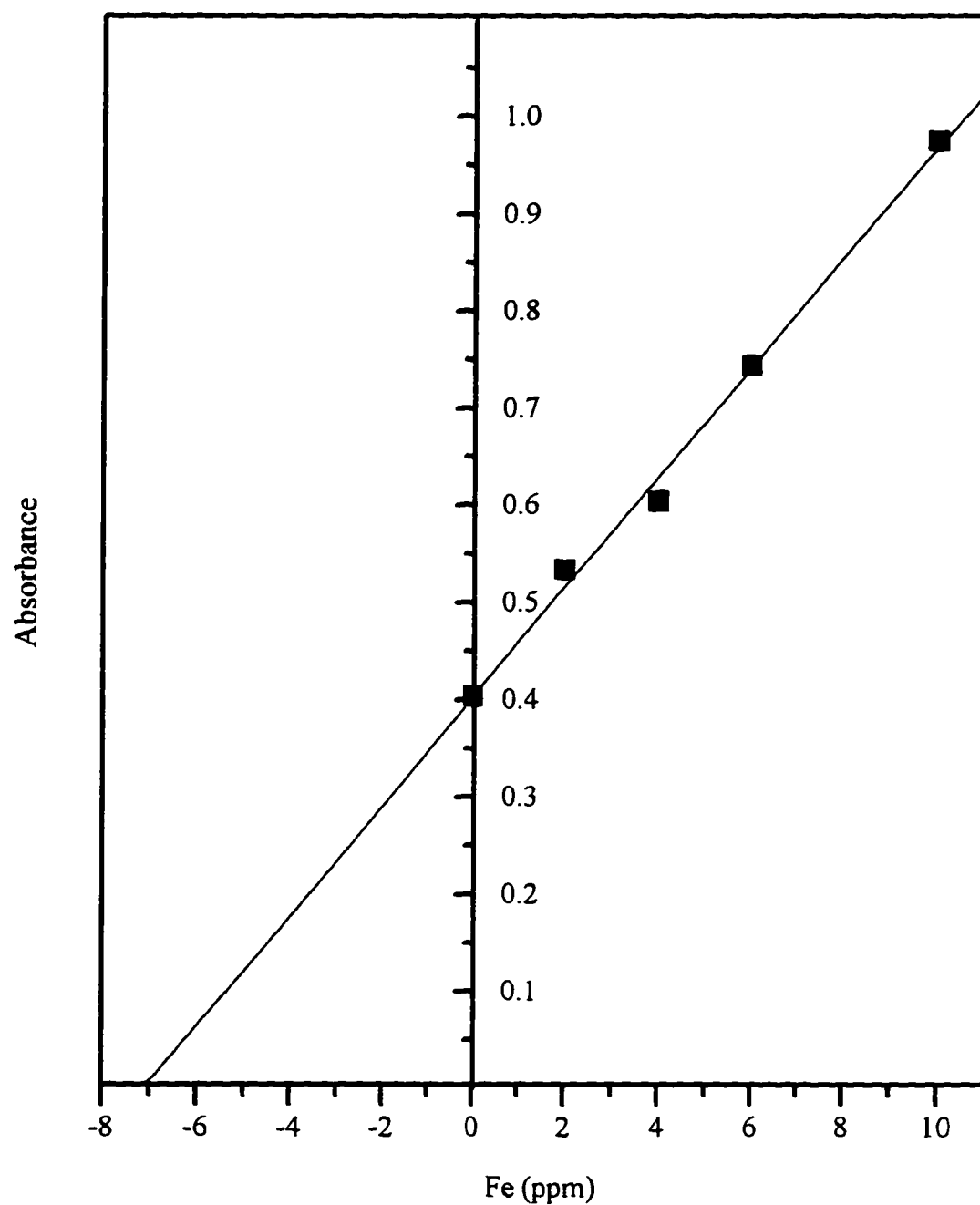


Figure 2.2 Typical standard addition method calibration curve for Fe.
All standards were mixed with sample 01C40 in a 1:1 ratio.

calibration curve of Fe is shown in Figure 2.2, and concentration was read by the instrument from the extrapolation of the calibration curve to the concentration axis.

The results listed in Table 2.3 are the average of four duplicate determinations by flame AAS performed one day, one week, two week, and one month after sample preparation using two calibration methods. The t-test results listed in Table 2.3 indicate that there is no significant difference between the external standard method and the standard addition method at greater than 99% confident level for 3 sets of samples. Figure 2.3 shows that the plots of Fe concentrations in compost-only leachates (Sample #C40) by the two different methods are in excellent agreement. Therefore the results for Fe, Mn, and Zn discussed below were obtained by the external standard calibration method except as otherwise indicated.

Table 2.3 The comparison of Flame AAS results using two calibration methods

Sample Name	Leach Day	Fe				Mn				Zn			
		Std Addition		External std		Std Addition		External std		Std Addition		External std	
		Method		method		Method		method		Method		method	
		Ave	%RSD	Ave	%RSD	Ave	%RSD	Ave	%RSD	Ave	%RSD	Ave	%RSD
		(n=4)		(n=4)		(n=4)		(n=4)		(n=4)		(n=4)	
		ppm		ppm		ppm		ppm		ppm		ppm	
01C40	1	7.04	1.2	6.98	0.7	1.367	0.9	1.352	0.6	1.053	1.7	1.069	1.3
05C40	6	12.67	0.9	12.80	0.9	0.355	1.3	0.358	0.5	0.802	1.9	0.793	0.9
10C40	13	4.74	0.9	4.78	1.1	0.270	1.5	0.274	0.8	0.263	2.0	0.266	0.7
15C40	32	5.25	1.2	5.19	0.7	0.298	1.3	0.293	1.2	0.510	2.1	0.501	1.1
24C40	93	4.87	1.0	4.90	0.6	0.138	1.6	0.140	0.9	0.199	2.3	0.204	1.5
01R40	1	2.27	0.8	2.30	0.8	0.042	1.3	0.043	1.3	1.222	2.1	1.211	0.6
04R40	5	4.42	0.9	4.38	0.5	0.156	1.1	0.158	1.1	0.712	1.8	0.704	0.9
09R40	21	2.45	1.0	2.47	0.9	0.220	0.7	0.217	0.7	0.322	1.2	0.327	1.1
13R40	45	2.08	0.8	2.11	1.1	0.258	1.5	0.261	0.9	0.590	1.7	0.600	1.3
18R40	85	1.79	1.2	1.77	0.8	0.222	0.9	0.220	0.8	1.570	1.1	0.155	0.7

Table 2.3

01TS40	1	0.092	1.2	0.091	0.9	1.353	1.6	1.369	0.8	0.604	0.9	0.596	0.7
04TS40	5	0.732	1.2	0.737	0.9	0.843	0.9	0.831	1.3	0.467	1.1	0.473	1.2
09TS40	21	2.010	0.9	1.988	0.6	0.897	1.3	0.904	1.1	0.419	1.3	0.422	1.2
13TS40	45	4.112	0.6	4.083	1.1	0.500	0.8	0.495	0.7	0.626	1.5	0.619	1.3
t-Test ¹ Confidence level		99.8%				99.8%				99.1%			

¹t-test confidence level: At which level there is no significant difference between the two methods

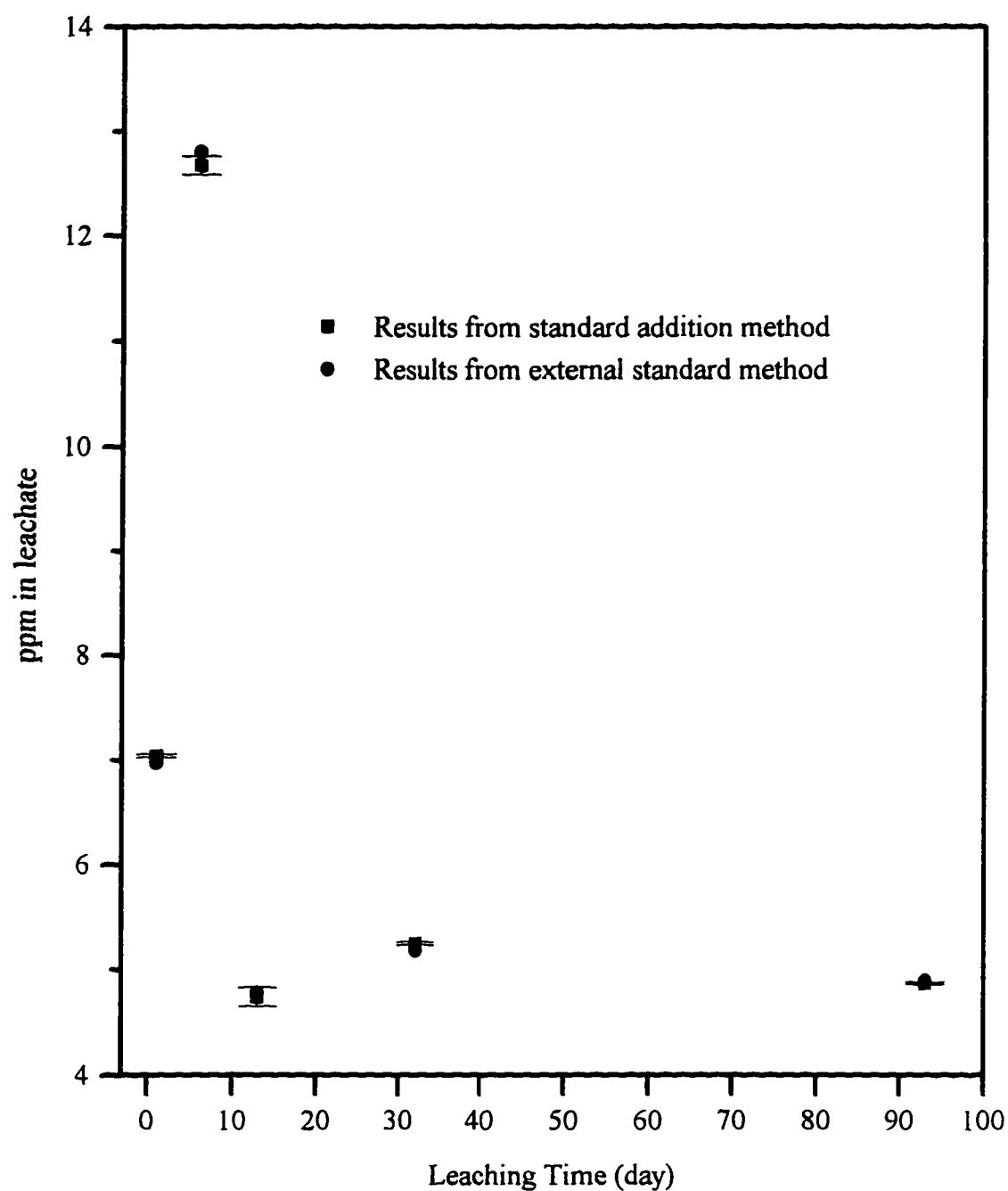


Figure 2.3 Comparison of results of Fe from standard addition and external standard calibration methods by Flame AA for sample C40. The difference between the two methods is well within the precision range of standard addition method. Data from Table 2.3

2.4 Analysis by Furnace AAS

The graphite furnace atomizer provides enhanced sensitivity over the flame atomizer because the entire sample in the furnace is atomized in a short period, and the average residence time of the atoms in the optical path is a second or more [45], about 10^3 times longer than the residence time of atoms in a flame. Atomization occurs in a cylindrical graphite tube which is open at both ends and has a central hole for introduction of sample by means of a micropipette or an autosampler. The tube is 28 mm long and has an internal diameter of somewhat less than 1 cm, which fits snugly into a pair of cylindrical graphite electrical contacts located at the two ends of the tube. These contacts are held in a water cooled metal housing. Two inert gas streams are provided. The external stream prevents the entrance of outside air and a consequent incineration of the tube. The internal stream flows into the two ends of the tube and out the central sample port. This stream not only excludes air but also serves to carry away vapors generated from the sample matrix during the first two heating stages.

Figure 2.4 illustrates the so-called L'vov platform, which is used in graphite furnaces in the Perkin Elmer HGA-40, shown in Figure 2.5. The platform is also graphite and is located beneath the sample entrance port. The sample is evaporated and ashed on this platform in the usual way. When the tube temperature is raised rapidly, however, atomization is delayed since the sample is no longer directly on the furnace wall. As a consequence, atomization occurs in an environment in which the

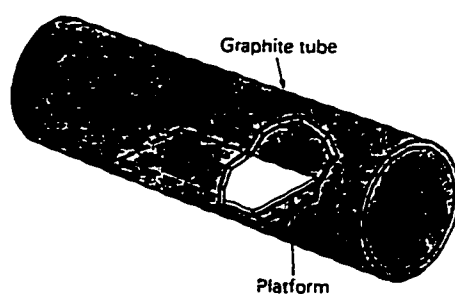


Figure 2.4 The L'vov platform inside graphite furnace tube
(from Reference 42)

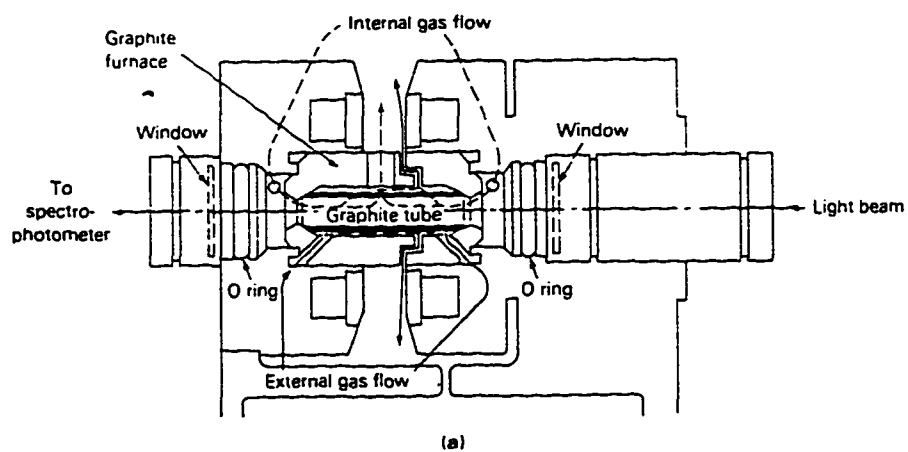


Figure 2.5 Cross-sectional view of the graphite furnace (from Perkin Elmer HGA-40 operating manual 1992)

temperature is not changing so rapidly that a non-isothermal atomization or volatilization may not take place. More reproducible peaks are obtained as a consequence. It has also been found that some of the sample matrix effects and poor reproducibility associated with graphite furnace atomization can be alleviated by reducing the natural porosity of the graphite tube. During atomization, part of the analyte and matrix apparently diffuse into the tube, which slows the atomization process and gives smaller analyte signals. To overcome this effect, most graphite surfaces are coated with a thin layer of pyrolytic carbon, which serves to seal the pores of the graphite tube.

2.5 Instrumental Conditions for Furnace AAS

A Perkin Elmer 3030B Atomic Absorption Spectrometer with a HGA-40 graphite furnace and AS-100 autosampler was employed in this project for trace elemental analysis of ppb levels of metals in leachates. Hollow cathode lamps, a deuterium background correction lamp, and pyrocoated graphite tubes (manufactured by CPI) were used for all elements. The manufacturer's recommendations for wavelength, slit band width, and lamp current parameters were followed [46]. The atomization temperature was calibrated for each element specified in Table 2.4.

In the leachate samples, complex matrixes affected the rate of analyte volatilization and caused vapor phase interferences as volatilization from the tube wall occurred under non-isothermal

conditions. The volatilization of the matrix also resulted in nonspecific absorption for which compensation was often inaccurate [47]. The presence of nonspecific absorption also resulted in decreased signal-to-noise ratios and therefore poorer detection limits. The problem was solved only when the atomization of analyte could be separated from the volatilization of the matrix using the temporal step-wise procedures together with modifiers discussed in the next section.

Table 2.4 Instrumental Conditions for GFAAS

Element	Smpl size μL	Modifier	Dry1			Dry2			Char			Atomize		
			T (°C)	Rmp (s)	Hld (s)	T(°C)	Rmp(s)	Hld(s)	T (°C)	Rmp (s)	Hld (s)	T (°C)	Rmp (s)	Hld (s)
Cd	40	5mL[0.015mg Pd & 0.01mg Mg]	100	10	60	130	40	10	750	30	30	1500	0	3
Cr	40		90	10	60	140	40	10	1200	30	30	2550	0	5
Cu	40		90	10	60	140	40	10	1000	30	30	2300	0	5
Ni	40		90	10	60	140	40	10	1300	30	30	2500	0	5
Pb	40	0.2mg PO ₄ /5mL	90	10	60	130	30	30	800	30	50	1900	0	3

Element	Wavelength (nm)	Slit setting	Standard 1 (ppb)	Standard 2 (ppb)	Standard 3 (ppb)
Cd	228.8	0.7	0.3	0.8	1.3
Cr	357.9	0.7	2.4	4.9	12.2
Cu	324.8	0.7	4.8	9.6	19.2
Ni	232.0	0.2	7.0	19.2	32.0
Pb	283.3	0.7	6.4	15.7	25.6

Rmp (s) = Ramp time in second, Hld (s) = Holding time in second

2.6 Drying Temperature and Time

The commonly recommended drying temperature and time [46], 120°C for 30 seconds in the first step of furnace program is used for simple inorganic matrixes with small sample sizes, i.e. 20 µl. However for leachates solutions from soil and sludge with volatile organics present and a larger sample size required for improving the detection limit, both volatile organics and water in contact with the surface of the L'vov platform in the tube will spatter at 120 °C, resulting in absorption peak splitting and degradation of accuracy and precision. Therefore a two-step drying program was devised. In the first drying step, the sample was heated up to 90 °C for 60 seconds to evaporate quietly most of the volatiles including water. In the second drying step, the temperature in the tube was slowly increased from 90 °C to 140 °C in 40 seconds. This step completely cleaned up the volatiles to ensure that no sample spatter occurred in the char step in which temperature is increased quickly from 140 °C to the char temperature. The drying temperatures and times for each element are listed in Table 2.4.

2.7 Char and Atomization Temperature and Matrix Modification

In leachates with high salt concentrations, a high char temperature is desirable to ensure removal of the matrix, but none of the elements of interest should be volatilized during the char step. While temperatures higher than 1000 °C can be used without loss of Cu, Cr, or Ni (Table

2.4), Cd and Pb may be partly or completely lost. Using a maximum char temperature of 550 °C (Figure 2.6), no loss of Pb was observed for standard solutions as shown in Figure 2.7. However a serious matrix interference occurred during atomization step for Pb with leachate sample 06CS40 (Figure 2.8) because in the char process the matrix was not completely destroyed. Among other interferences is a broad-band molecular absorption resulting from incomplete breakdown of the matrix in the brief time during which atomization takes place [48]. In samples containing halogens, stable metal halides such as CaCl_2 , NaCl , and KCl can be found to exist in atomization steps if they are not burned in the char step [49]. These species exhibit broad absorption bands in the ultraviolet. Scattering by incompletely decomposed organic particles also occurs commonly [50]. Furthermore, these hot gaseous media are usually highly inhomogeneous both as to chemical composition and particulate distribution, and thus cause the continuous deuterium lamp background corrector to function erroneously. This situation could be improved if a proper temperature program is used and suitable matrix modifiers are chosen.

When palladium and magnesium (prepared from 10% of $\text{Pd}(\text{NO}_3)_2$ solution and 10% of $\text{Mg}(\text{NO}_3)_2$ solution manufactured by CPI) were directly added to the furnace by the autosampler, the atomization temperature for Cd was increased to 1500 °C (Figure 2.9). Therefore 750 °C can be used for char temperature to destroy the matrixes, without loss of Cd. However, when this combination of modifiers is applied to the Pb determination, the optimum atomization

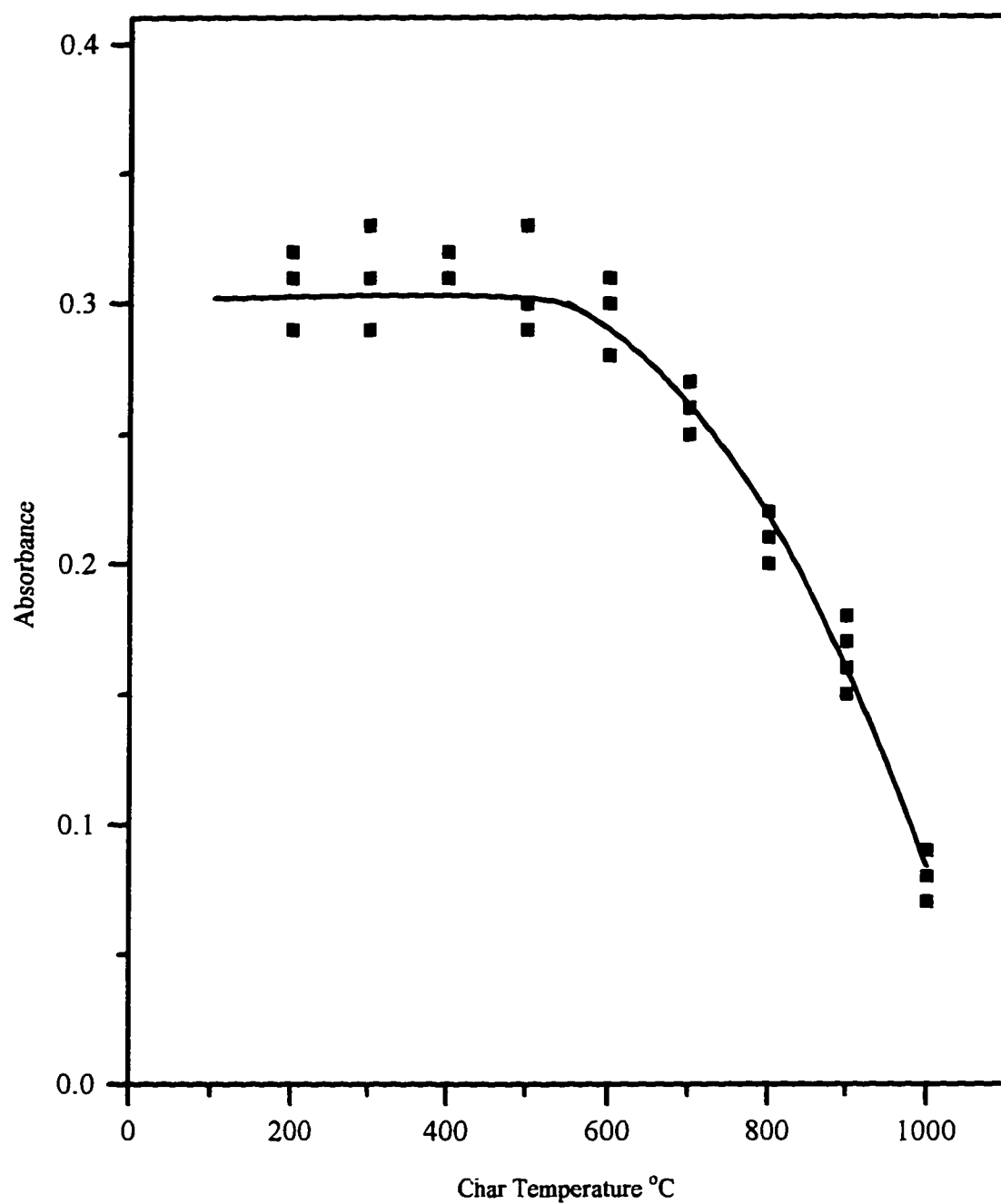


Figure 2.6 Maximum char temperature for Pb without modifier. 20ppb Pb standard; atomization temperature, 1600°C; absorbances read from atomization step at 283.3nm.

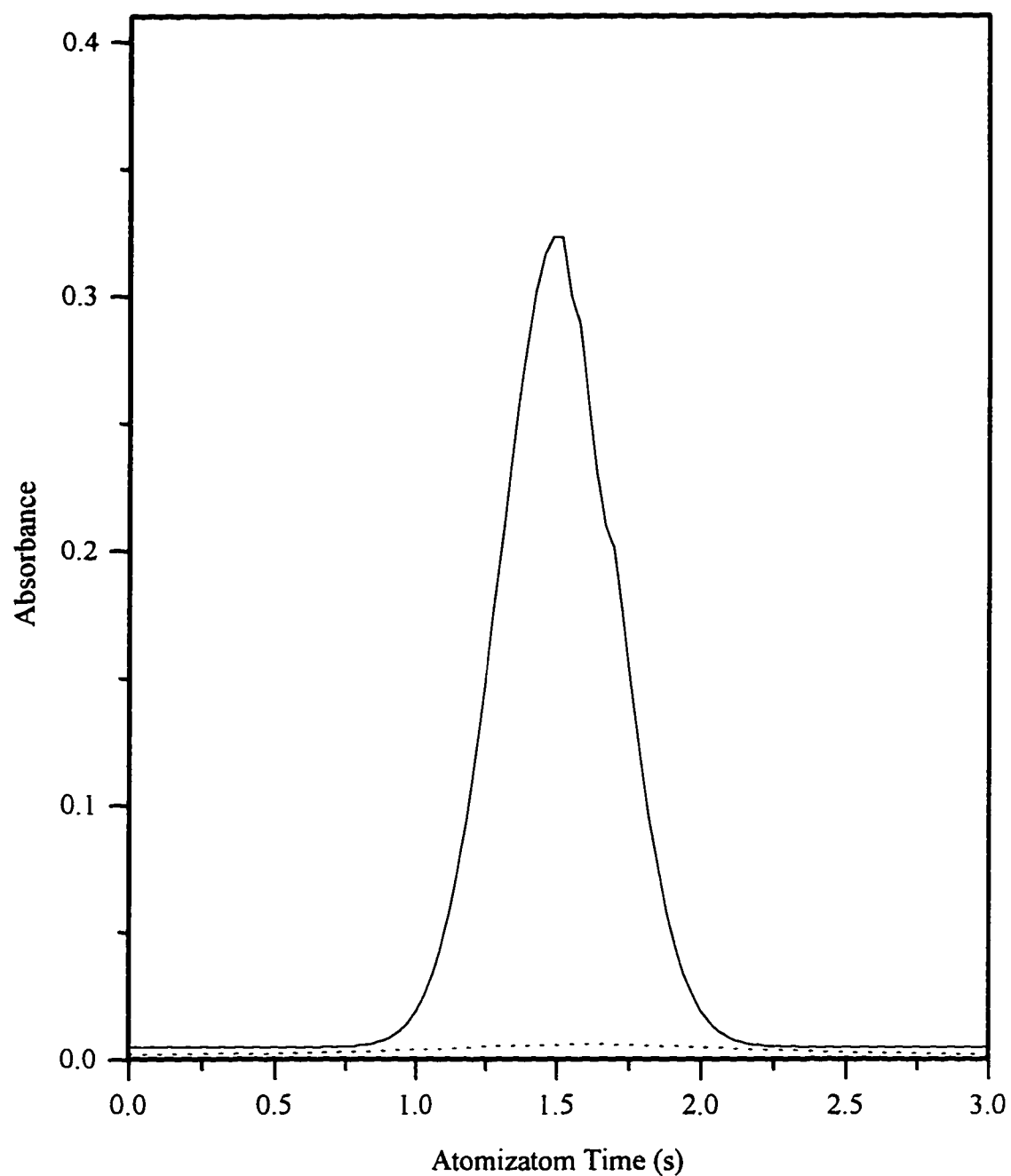


Figure 2.7 Plot of Atomization of 20ppb Pb Standard Solution with Char temperature 550°C and atomization 1600°C.

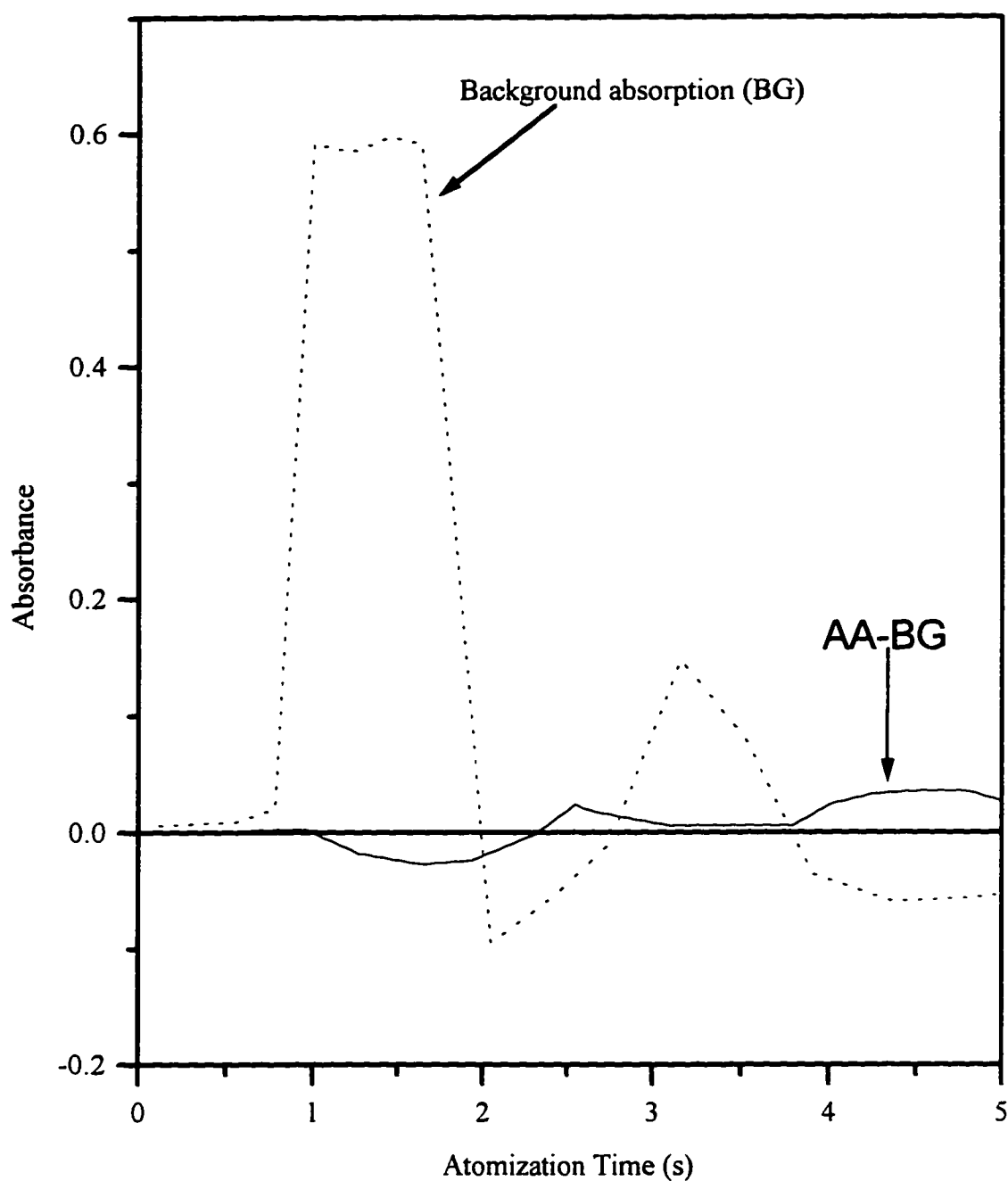


Figure 2.8 Plot of atomization profile with leachate sample 06CS40 containing 18.5ppb Pb, char temperature 550°C, and atomization temperature 1600°C. Absorbance at 283.3nm.

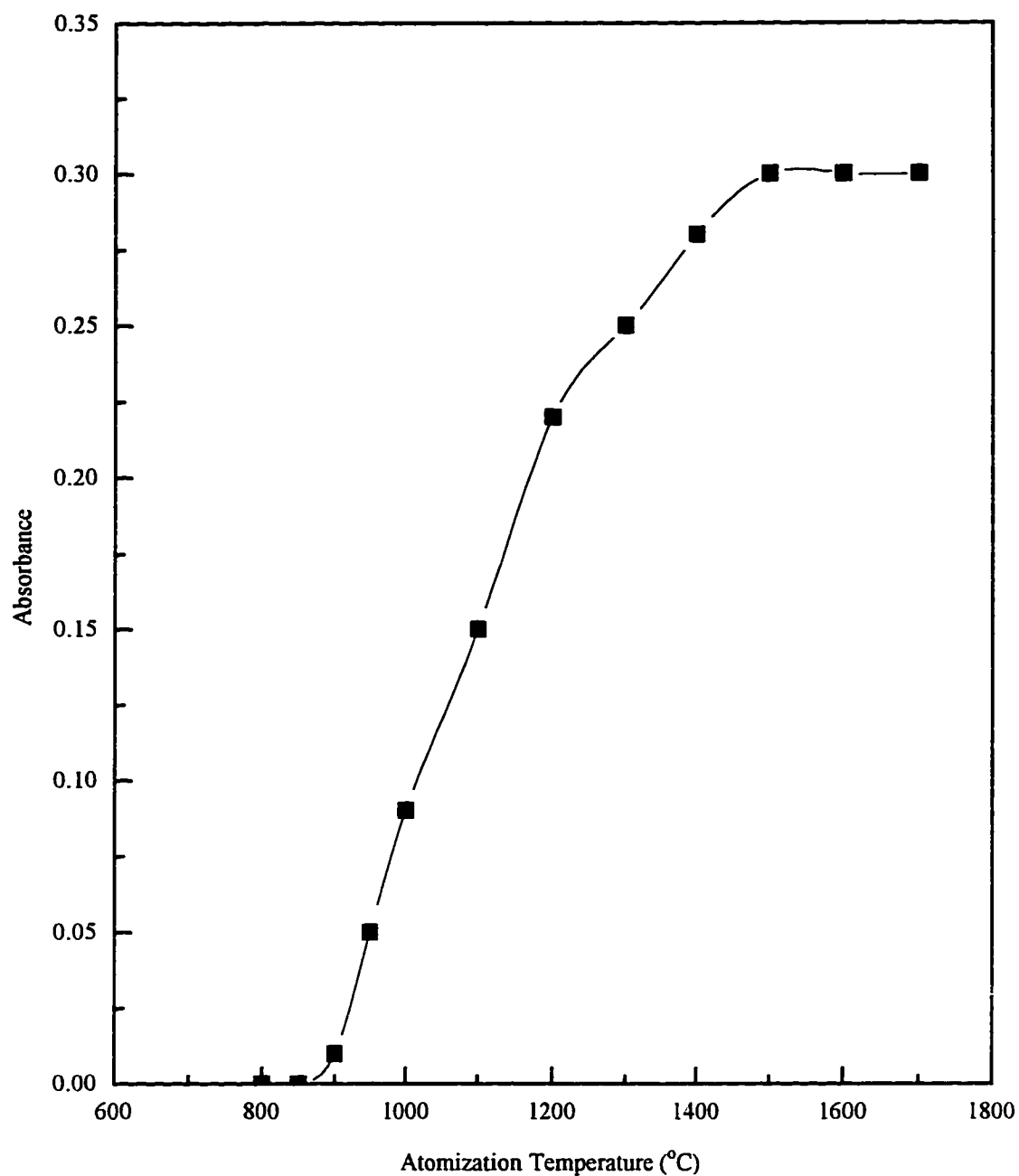


Figure 2.9 Optimum Atomization Temperature for Cd with Mg-Pd Modifier, Sample 03CR40 containing 1.2ppb Cd, char temperature 750°C, absorbance at 228.8nm for Cd.

temperature was not reached until 2200°C (Figure 2.10). However, at 2200°C, a heavy smoke occurred due to the atomization of the Mg bulk modifier. This smoke scatters the Pb and deuterium light [51], and hence precludes the determination of Pb (Figure 2.11).

With $\text{NH}_4\text{H}_2\text{PO}_4$ as modifier (ACS reagent, from Aldrich), the atomization temperature for Pb was increased to 1900 °C (Figure 2.12). However, a longer than usual char time (50 seconds) at 800 °C was needed to remove both the original matrix and most of the added modifier $\text{NH}_4\text{H}_2\text{PO}_4$ (Figure 2.13C). Otherwise heavy smoke due to phosphate volatilization would be observed in atomization step for Pb (Figure 2.13A & B) and the strong background absorption will cause the deuterium background correction to be in error.

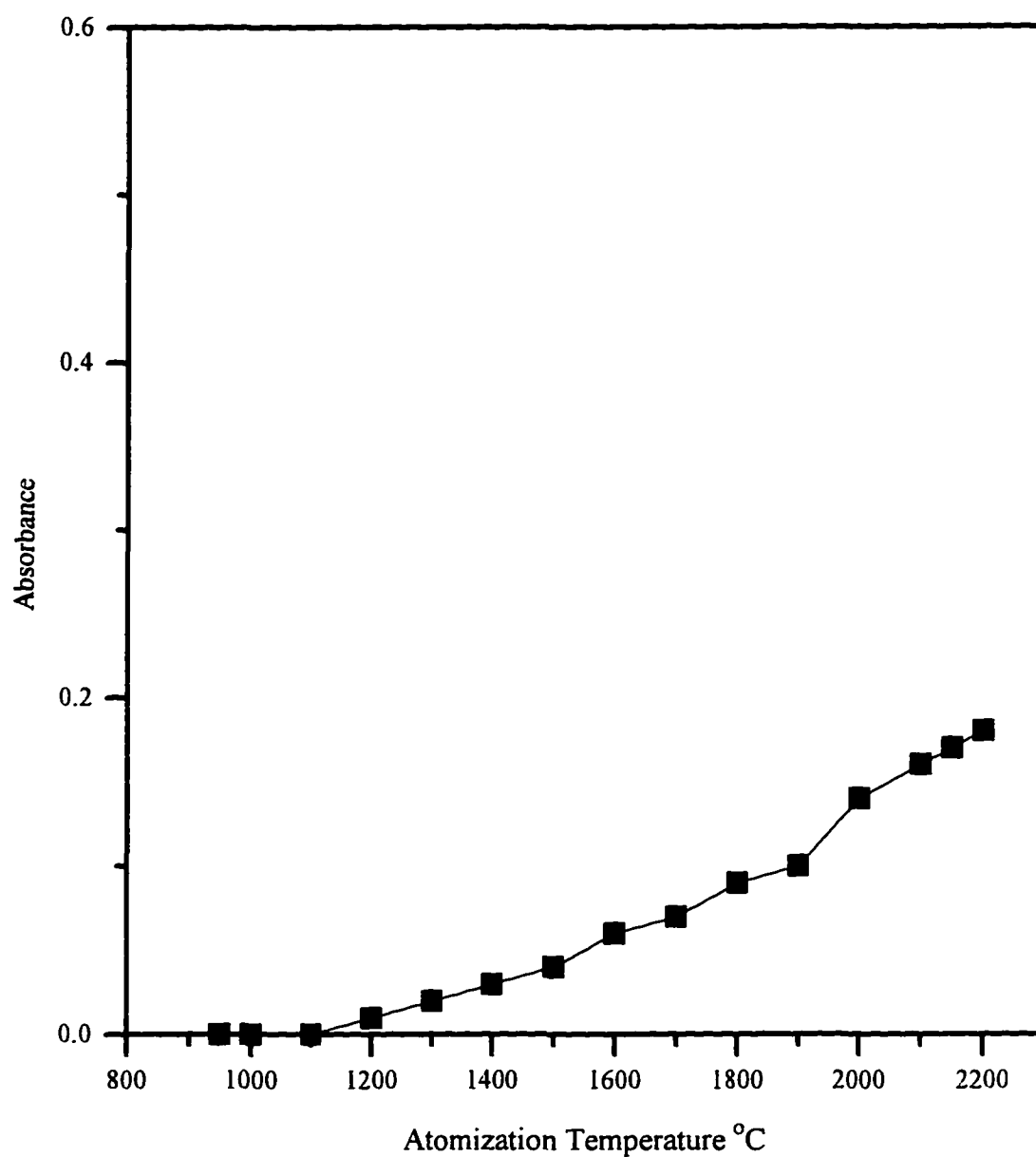


Figure 2.10 Atomization temperature of Pb with Pd-Mg modifier.
Sample 06CS40, 18.5ppb Pb, Char temperature 1000°C for 30s.
Serious smoke condition occurred for temperature over 2200°C
due to atomization of Mg and other components.

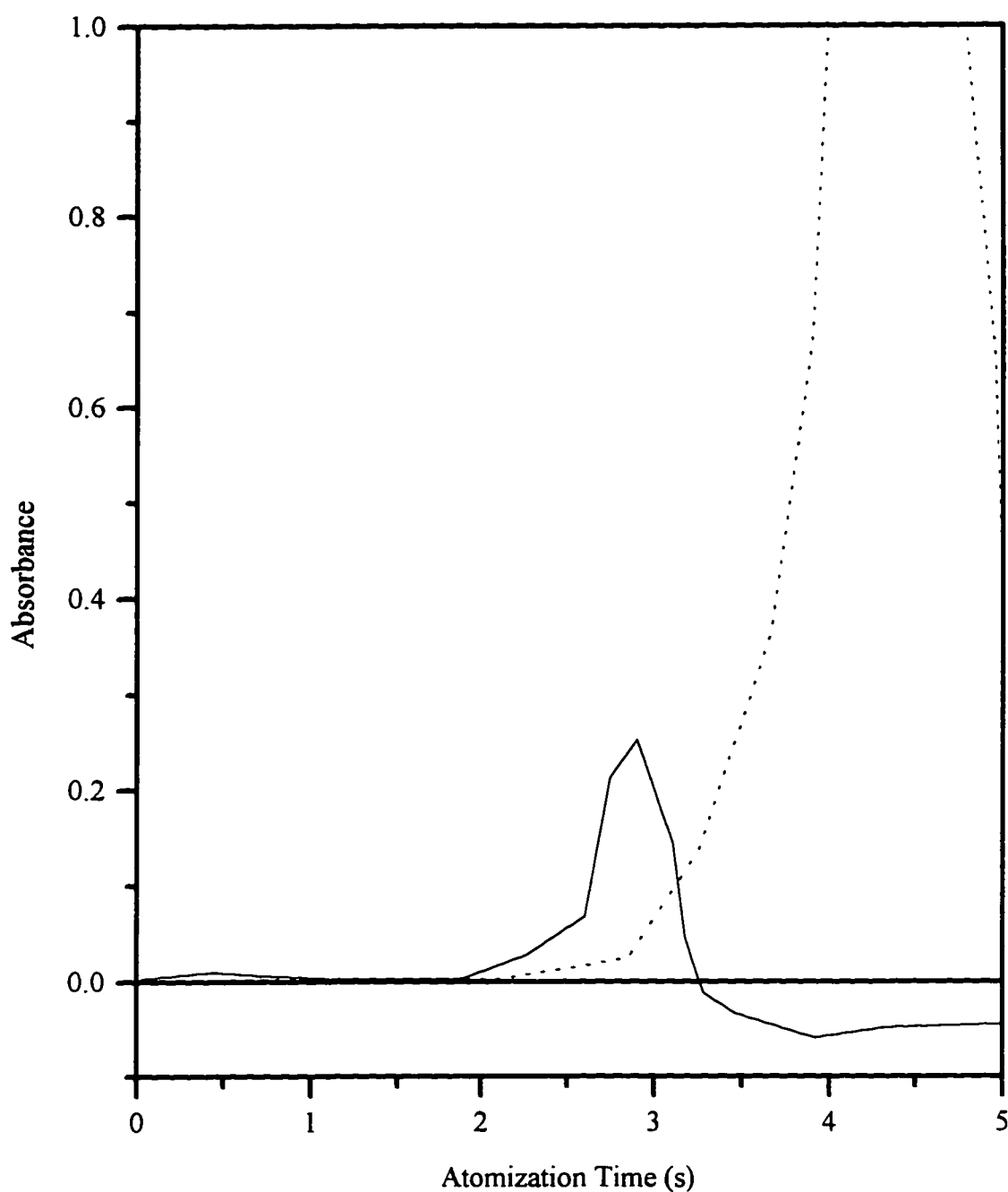


Figure 2.11 Atomization profile of sample 06CS40 (18.5ppb Pb) with Pd-Mg modifier, char temperature 1000°C, atomization temperature 2200°C. Solid line = Pb absorbance signal; dotted line = deuterium background correction signal

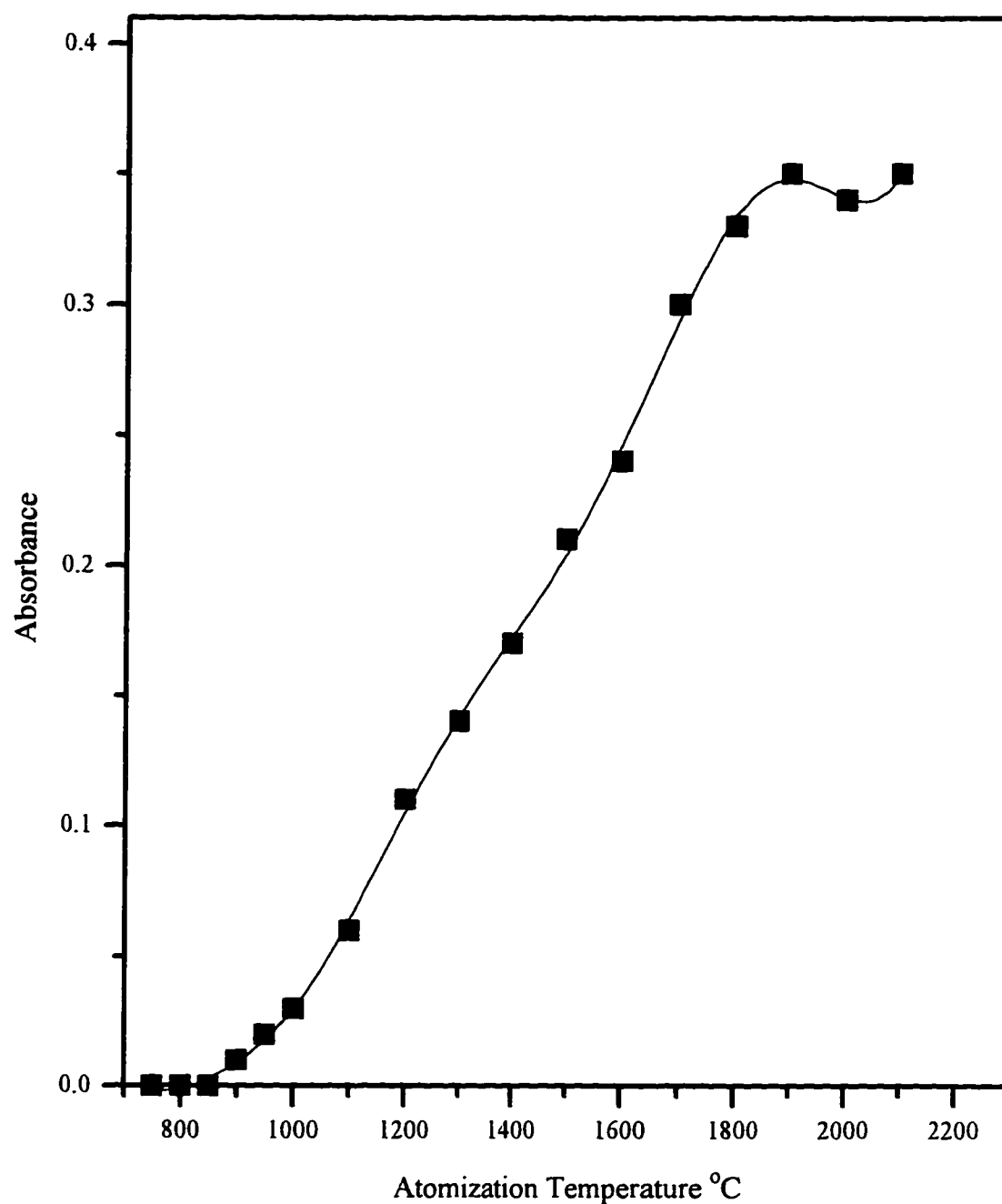


Figure 2.12 Optimum atomization temperature for Pb with $\text{NH}_4\text{H}_2\text{PO}_4$ modifier, Sample 06CS40 (18.5ppb Pb), char temperature 800°C for 50s.

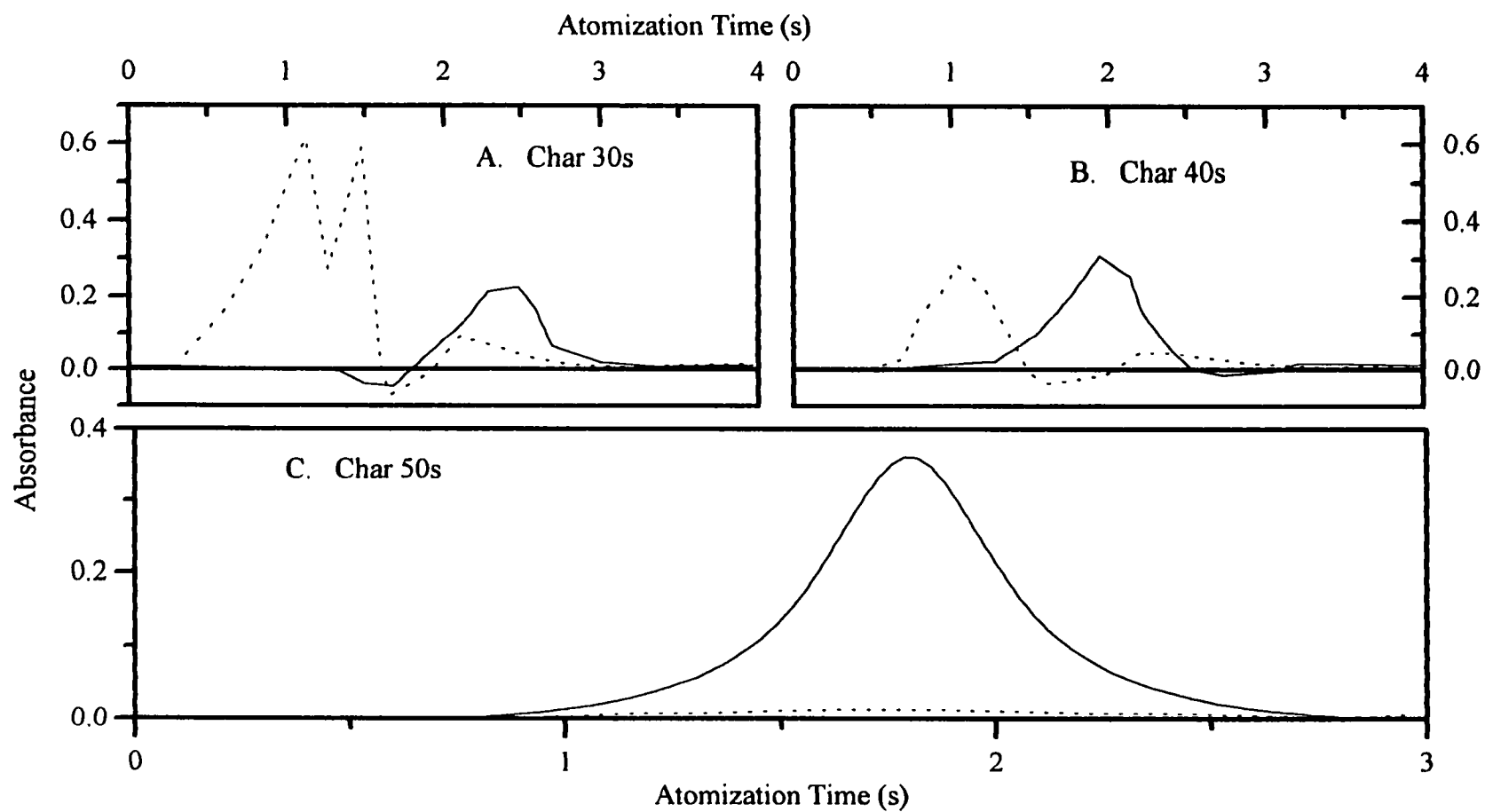


Figure 2.13 Effect of char time on the profiles of atomization of sample 06CS40, $\text{NH}_4\text{H}_2\text{PO}_4$ modifier, char temperature 800°C , atomization temperature 1900°C . Solid line = Pb absorbance signal; dotted line = deuterium background correction signal.

2.8 Standard Addition Method

In flame AAS, the standard addition method is often helpful in counteracting matrix effects when preparation of standards that match the samples is impossible or extremely difficult, such as in the analysis of complex materials. However, the standard addition method provides fewer advantages to GFAAS when the temperature program together with modifiers is optimized to remove most of the matrix before atomization. Table 2.5 lists the precision for selected samples in determination of Fe, Cu, and Pb by external standard calibration and standard addition methods. It is worthwhile to note that the standard addition method improves the precision only a small amount for Pb, and even less for Fe and Cu, in which the complicated sample preparation procedures in the standard addition method may worsen the precision. Because of the higher char temperature for Fe and Cu, the matrix effects were completely eliminated before atomization of Cu and Fe in both calibration methods. Therefore external standard methods with simplicity for Fe and Cu show better precision than the standard addition method.

Table 2.5 Precision of Standard Addition Method and External Standard Calibration Methods (n=7) Conditions are listed in Table 2.4

Sample Name	Fe		Cu		Pb	
	Std Addition	Non-Std Addition	Std Addition	Non-Std Addition	Std Addition	Non-Std Addition
01C40	1.1	0.6	1.2	0.8	3.2	3.5
05C40	1.3	0.9	1.5	0.7	3.8	4.1
10C40	0.9	0.7	1.2	1.1	4.2	3.2
15C40	1.3	1.2	1.5	0.9	3.1	3.9
24C40	1.0	0.8	1.3	0.9	2.9	4.0
01R40	1.3	1.0	1.7	1.2	3.7	4.1
04R40	0.9	0.7	1.3	1.0	3.2	4.3
09R40	1.6	0.9	1.4	0.7	3.1	3.6
13R40	1.3	1.1	1.2	0.9	2.7	3.1
18R40	1.4	0.7	1.3	1.2	3.5	4.0
01TS40	1.5	1.3	1.0	0.8	2.6	3.9
04TS40	1.2	1.0	1.3	0.5	2.9	3.2
09TS40	0.9	0.6	1.2	1.0	2.3	2.9
13TS40	1.3	0.8	1.1	0.9	3.2	3.5

Chapter 3 Elemental Analysis by ICP-AES

3.1 Introduction

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) is one of the more reliable analytical techniques, applicable to different samples such as ores, ferrous alloys, rare earths, seawater, fresh and waste waters, soils and sediments, biological fluids, and organic materials, for the determination of about 75 elements [52-55]. The plasma source offers several benefits compared with the flame and electrothermal (graphite furnace) methods. Among its advantages is fewer interelement interferences, which is a direct consequence of its higher temperatures. Second, good spectra can be obtained for most elements under a single set of excitation conditions. This property is of particular importance for the multielement analysis of small samples. Flame and electrothermal sources are less satisfactory in this regard because optimum excitation conditions vary widely from element to element. Plasma source often permit the determination of an element over several decades of concentration range in contrast to one or two for FAAS and GFAAS. Finally, perhaps the most important is the much great reproducibility of atomization conditions, which often leads to precisions that are better by a factor of ten or more.

Figure 3.1 is a schematic drawing of an inductively coupled plasma source. It consists of three concentric quartz tubes through

which streams of argon flow at a total rate between 11 and 17 liter/min. Surrounding the top of this tube is a water-cooled induction coil that is powered by a radio-frequency generator, which is capable of producing 2KW of energy at about 27 MHz. Ionization of the flowing argon is initiated by a spark from a Tesla coil. The resulting ions, and their associated electrons, then interact with the fluctuating magnetic field produced by the induction coil. This interaction causes the ions and electrons within the coil to flow in the closed annular paths depicted in Figure 3.1; ohmic heating is the consequence of their resistance to this movement.

The analyte solution is carried into the spray chamber through the nebulizer by a peristaltic pump. The pneumatic nebulizer used in our instrument is the glass Meinhard dual concentric type (Figure 3.2). After it is pumped into the nebulizer, the stream of sample solution is disrupted by the high velocity gas flow (Ar carrier gas) to produce a spray of droplets with diameter less than 10 μm (aerosols), which is carried into the plasma. Also used in our experiment is an ultrasonic nebulizer (USN). With an ultrasonic nebulizer, the sample is delivered to a piezoelectric transducer which vibrates at an ultrasonic frequency between 200 KHz and 10 MHz. This mechanical force breaks the sample into much finer and more uniform droplets than does the pneumatic nebulizer system. In fact the aerosol formation by the ultrasonic nebulizer is so efficient, that a desolvation process with Peltier cooling is normally required to remove the solvent vapor. Since

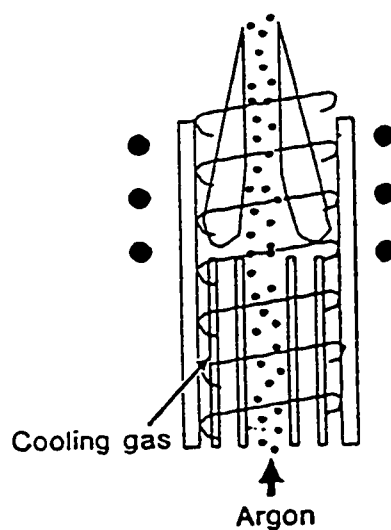


Figure 3.1 A typical inductively coupled plasma source
(from Reference 54)

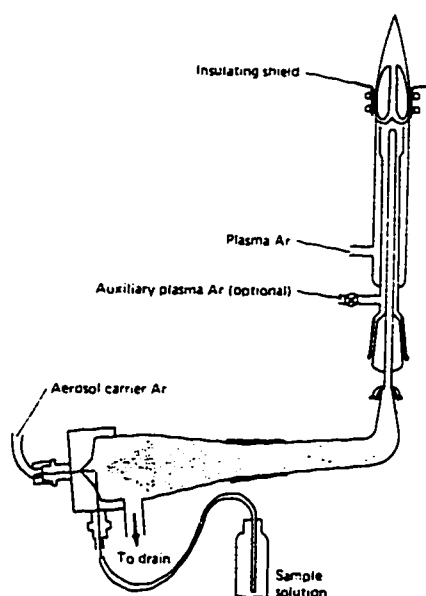


Figure 3.2 The Meinhard concentric pneumatic nebulizer
(from Reference 56)

the production of aerosol is very efficient and is independent of the gas flow, more analyte can be transported to the ICP at a slower rate of injection gas than can be achieved with a pneumatic nebulizer, thus giving longer residence times for analytes in the plasma and subsequently a greater number of emitting species. It is reported that detection limits with the USN are normally about 10 times better than with a conventional pneumatic nebulizer [57-59]. However, salt buildup on the injector tube orifice will be increased, when solutions having high salt concentrations are nebulized, which may decrease the determination precision. In this research, all studies used USN except as otherwise indicated.

Figure 3.3 shows temperatures in various parts of the plasma. By the time the sample atoms have reached the observation point, they will have resided for about 2 millisecond at temperatures ranging from 6000K to 8000K. These times and temperatures are roughly two to three times greater than those found in the hotter combustion flames employed by flame methods. Therefore, atomization is more complete and fewer chemical interference problems arise.

The benefits of the ICP stem not only from the very high temperature of the source, but also the unique method of heating the sample. The sample is introduced along a central tunnel and the temperature in this tunnel, although sufficient to volatilize and atomize the sample, is nevertheless relatively cool in comparison to the surrounding toroidal plasma. The sample is therefore heated from the

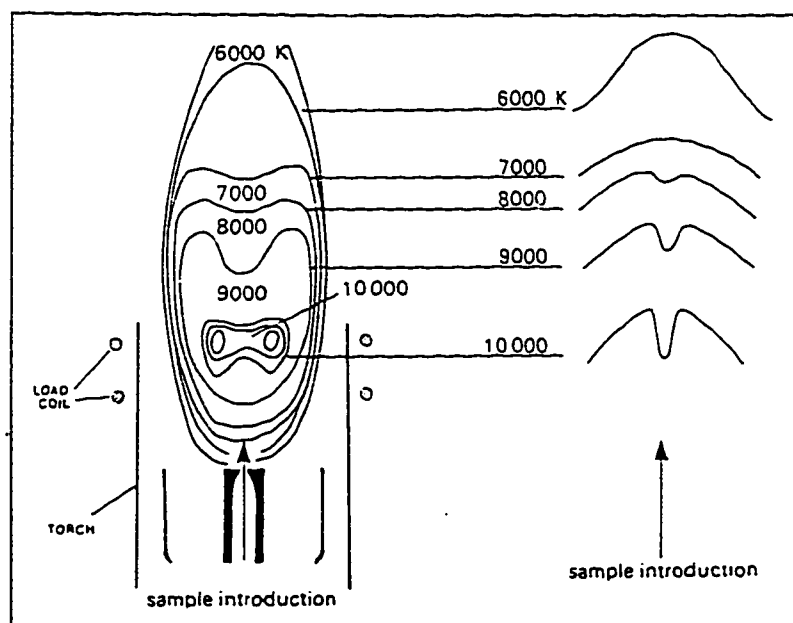


**Figure 3.3 Plasma temperature distribution in ICP source
(from Reference 63)**

outside by the plasma, with a broad temperature profile within the tunnel (Figure 3.3). This unique method of heating allows ICP to avoid self-absorption and self-reversal effects. Therefore, the dynamic range of ICP calibration is much higher than flame, furnace and any other sources.

3.2 Experimental Conditions in ICP-AES

A SpectroFlame Modula ICP-AES system with two monochromators was used. One monochromator is used to cover the UV range from 160 to 440 nm and the another covers from 240 to 800nm. The USN unit was a Spectrosonic, which was made by Spectro specifically to connect to the ICP system. The operating parameters of the ICP-AES and USN were adjusted to conditions under which the sensitivity was highest (Table 3.1). The analytical lines which gave the highest sensitivity and least interferences from others were experimentally chosen from the prominent lines listed in Table 3.2.

Table 3.1 Instrumental and operating parameters

ICP-AES	Spectroflame Modula
RF power	1.2 KW
Coolant gas	12 L/min.
Auxiliary gas	1 L/min.
Nebulizer gas	1 L/min.
Observation height	14mm above work coil
Integration time	varied with elements (see Table 3.3)
Spectrometer	twin monochromator
Mount	cross Czerny, 2-channel
Focal length	0.75 m
Gratings	channel 1, N ₂ filled, with 3600 grooves per mm ruled grating
	channel 2 with 2400 grooves per mm holographic grating
Slits	25 μ m for channel 1 and 2
Torch	fixed three tubes torch
USN	Spectrosonic
Nebulizer gas	0.5 L/min.
peristaltic pump rate	2 mL/min.
sample gas flow	0.8 mL/min.
Heater temperature	150 °C
Coolant temperature	4 °C

3.3 Standard preparation and analyte line selection

Six types of mixed standard solutions were prepared to construct the calibration curves for major elements from the stock solutions (see Section 2.3). The compositions of the mixed standard solutions are shown in Table 3.3. They were prepared in such a way as to cover the concentration range of most of the samples, and at the same time, to keep the concentration of each solution nearly equal. However, the lowest concentration for element standard is determined by instrument detection limits (see Section 3.5).

Each wavelength in Table 3.3 was selected from several prominent spectral lines listed in Table 3.2 using the following criteria: 1) prominence of the line, 2) freedom from spectral interferences, 3) sufficient range of linearity, 4) practical utility in the specific situation. An experimental profile of the spectral region surrounding the analyte line is obtained following the choice of line based on signal level (intensity and sensitivity) (Table 3.2), or S/N, detection limit (discussed in the following sections), and proximity of matrix constituents (Figure 3.5 to Figure 3.10). Both standards and samples to be analyzed were used to determine the profiles. Observable spectral and background interferences, their levels, and their reproducibility were evaluated.

Table 3.2 Some Prominent Spectral Lines from an Argon ICP [44]

Element	Wavelength (nm)	Sensitivity (Intensity x 1000/ppm)	B.E.C. ¹ (ppm)	Possible Interference
As	228.812	36.0	2.10	Fe, Ni
	193.696	6.5	2.3	
	188.979			Cd
Cd	228.802	1400	0.07	Al, Fe, Ni
	226.506	1000	0.1	Fe, Ni
	351.051	135.0		
Cr	283.563	3700	0.14	Fe, Mg, V
	284.352	2600	0.19	
	267.716	2200	0.18	Fe, Mn, V
Cu	324.754	8000	0.08	Ti
	327.396	4000	0.16	Ca, Cr, Fe
	223.008	190	0.53	
Fe	259.940	7000	0.06	
	238.204	3500	0.08	Cr, V
	273.955			Mn, Ti
Mn	257.610	18000	0.02	Al, Cr, Fe, V
	259.373	13000	0.02	Fe
	293.930	4600	0.08	
Mo	379.825	2400	0.33	
	313.259	1800	0.44	
	202.030	155	0.52	
Ni	352.454	1600	0.3	Fe
	341.476	1400	0.3	
	231.604	620	0.25	
Pb	283.306	340	1.4	Cr, Fe, Mg
	220.353	150	0.55	
	216.999			
Se	196.026	11	5.7	
	185.520			
	185.880			
Zn	213.856	1020	0.08	
	330.2259	50		Al, Cu, Fe
	481.053	45		
Y	378.870			
	377.433			Fe, Mn, Ti, V
	371.030			Ti, V
	360.073			Mn
	361.105			

¹B.E.C --- Background Equivalent Concentration

Table 3.3 Standard solution (ppb) and element parameters

Analyte Line (nm), (Integration time)	DL (ppb)	STD1	STD2	STD3	STD4	STD5	AIDL (ppb)
As 1888.979 (30s)	4	30	50	15	5	10	3
Cd 226.502 (20s)	0.6	4	7	28	1	14	0.2
Cr 284.325 (10s)	1.4	50	9	20	100	4	0.9
Cu 324.754 (6s)	0.4	200	100	50	500	2	0.3
Fe 259.940 (3s)	0.3	10000	5000	1000	80	45	0.3
Mn 293.930 (3s)	0.2	800	1500	200	20	45	0.2
Mo 202.030 (15s)	1.2	360	20	5	150	3.5	1
Ni 231.604 (10s)	1	45	200	90	20	5	0.8
Pb 220.353 (20s)	2	20	50	200	15	10	2
Se 196.026 (20s)	2	10.8	18	24	3.6	8.4	1
Zn 213.856(3s)	0.5	200	800	1500	5	20	0.4

DL ---- Detection Limit for selected integration time

AIDL ----- Absolute Instrumental Detection Limit

3.4 Background Correction

Although the background correction in ICP is not so critical as in furnace AAS analysis, in which the analyte signal can be completely masked out by the matrix (see Figure 3.4), background correction in ICP can improve further on the stability and accuracy of the results, especially for the sewage and soil leaching samples, for which an ideal matrix match for standards is impossible. As shown in Figure 3.8 the raw intensity for Cd in leaching sample 01T40 subsequently determined to be 7 ppb is obviously different from the standard 7ppb Cd solution because of the different background intensities of the standard and sample. However, after background correction, the same net signal intensities are obtained from both.

As shown in Figure 3.4 with the scanning monochromator, a series of short integrations is made over a spectral region about ± 0.05 nm in the vicinity of the analyte line. The background intensity is estimated by interpolation of outlying off-peak measurements,

$$I_U = I_{UL} + (I_{UR} - I_{UL}) \times a/(a+b) \quad (3.1)$$

and the intensity difference at the peak wavelength is,

$$I_N = I_R - I_U \quad (3.2)$$

Where I_N is the net intensity, I_U is the background intensity at signal position, I_{UR} and I_{UL} are intensities at the right and left background positions, a and b are the distances of the background positions from peak maximum on left and right, respectively.

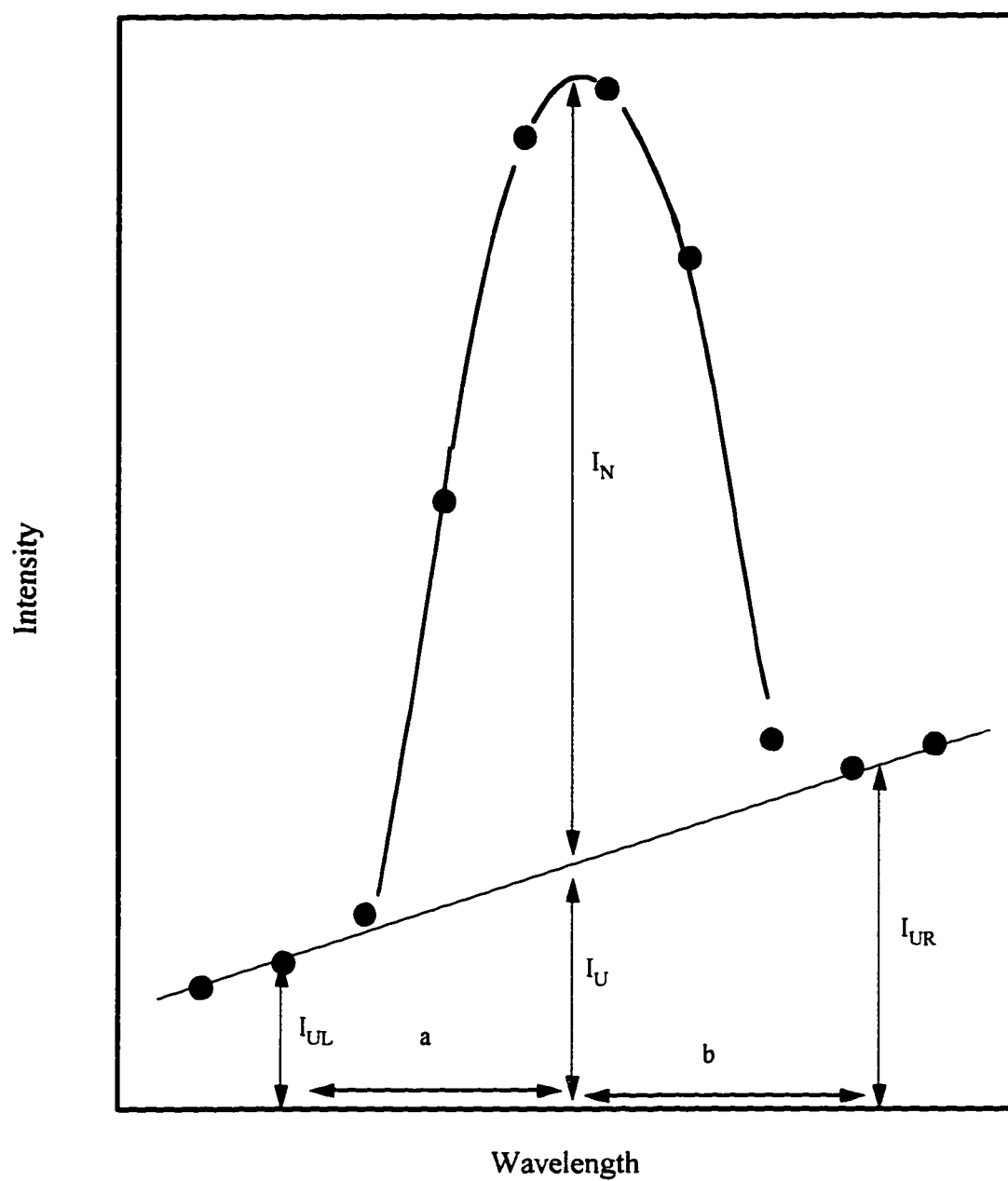


Figure 3.4 Method of estimating the analyte peak net intensity, I_N , from scan data

The spectral profiles for background correction positions were determined by the wavescan mode of the instrument software. For each analyte line, three solutions were run at the same integration time as that in the sample analysis mode listed in Table 3.3 (to be discussed in the following sections). One solution is a standard with a medium concentration, the second is a leachate solution with the lowest concentration close to 5 times of detection limit for that analyte line. The third is a leachate solution with a high concentration of the element of interest. The selection of a sample solution with a low concentration ensures that a genuine peak is present. When the spectrum of a standard is compared with that of the sample, any obvious interference and wavelength drift can be recognized to adjust the background correction positions. For example, as illustrated in Figure 3.5, a correction position for a small peak may be proper for a low concentration standard (points A and B), that position may just extend to the shoulder of a higher concentration standard peak. Therefore the spectrum of a sample with a high concentration is needed to adjust the background correction positions (points C and D). In some cases as shown in Figures 3.5 to 3.7, longer integration times are needed for those samples with the lowest concentrations in order to significantly distinguish the small peaks from the background. The background correction positions are shown as vertical dotted lines for all 11 analyte lines in the spectra in Figures 3.5 to 3.10.

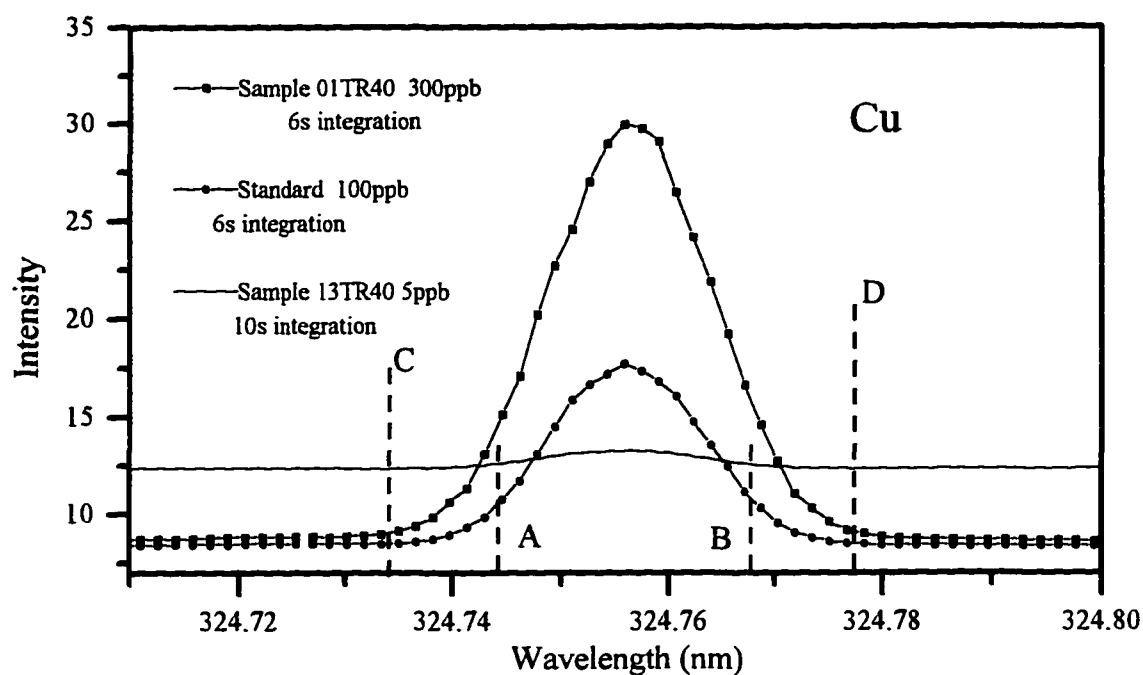


Figure 3.5 Background correction positions for Cu spectra, with standard and samples. Background positions A and B may be suitable for sample 13TR40 containing 5ppb Cu, but not for sample 01TR40 containing 300ppb Cu. Positions C and D are suitable for samples containing low and high concentrations

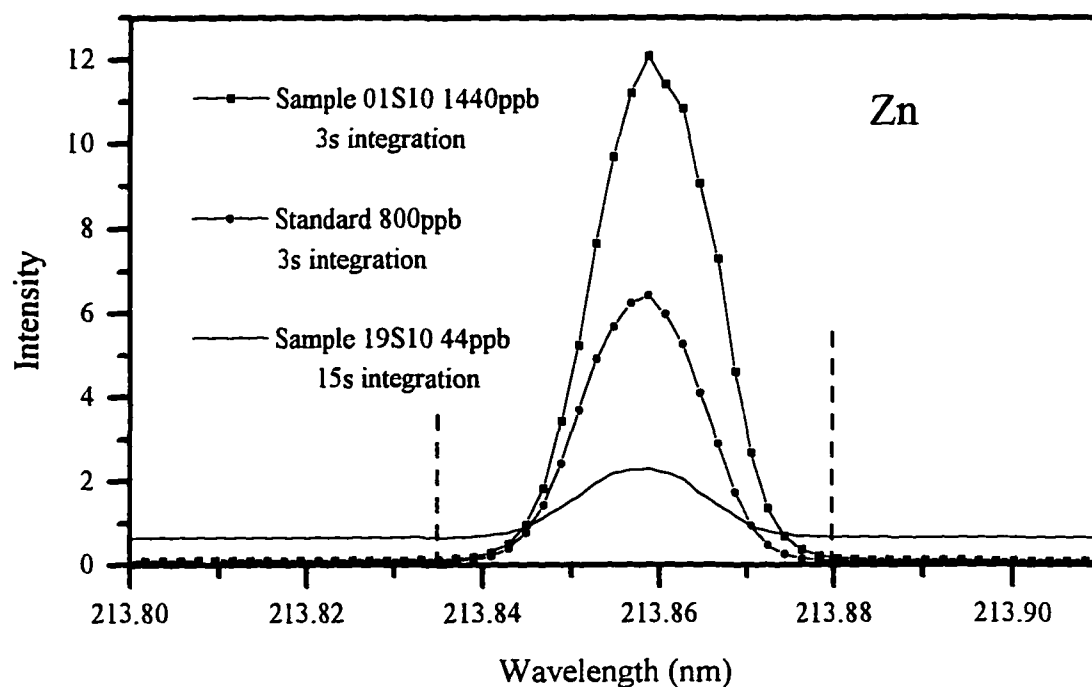


Figure 3.6 Background correction positions for Zn surrounding 213.856nm.

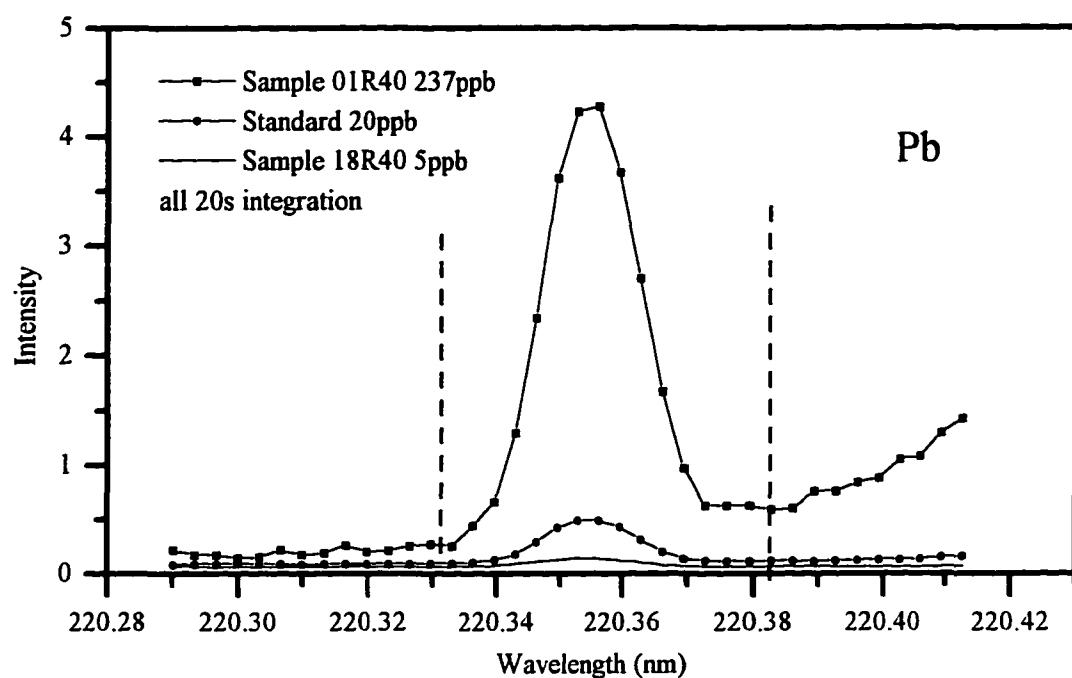


Figure 3.7 Background correction position for spectra of Pb around 220.353nm.

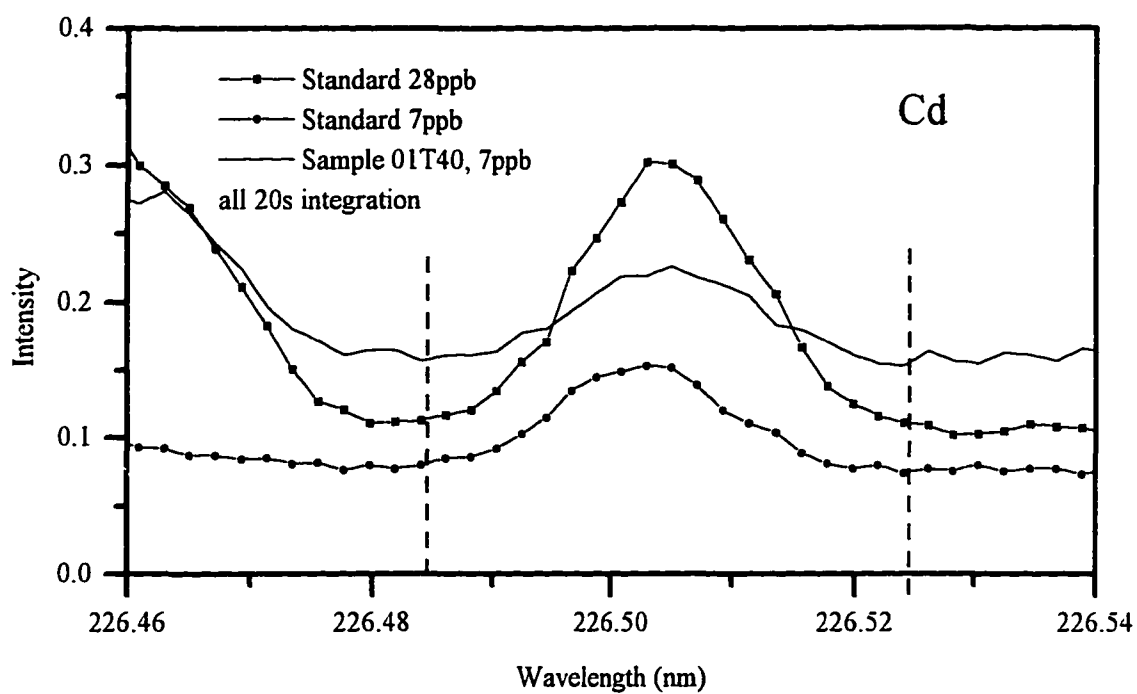


Figure 3.8 Background correction positions for Cd surrounding 226.502nm.

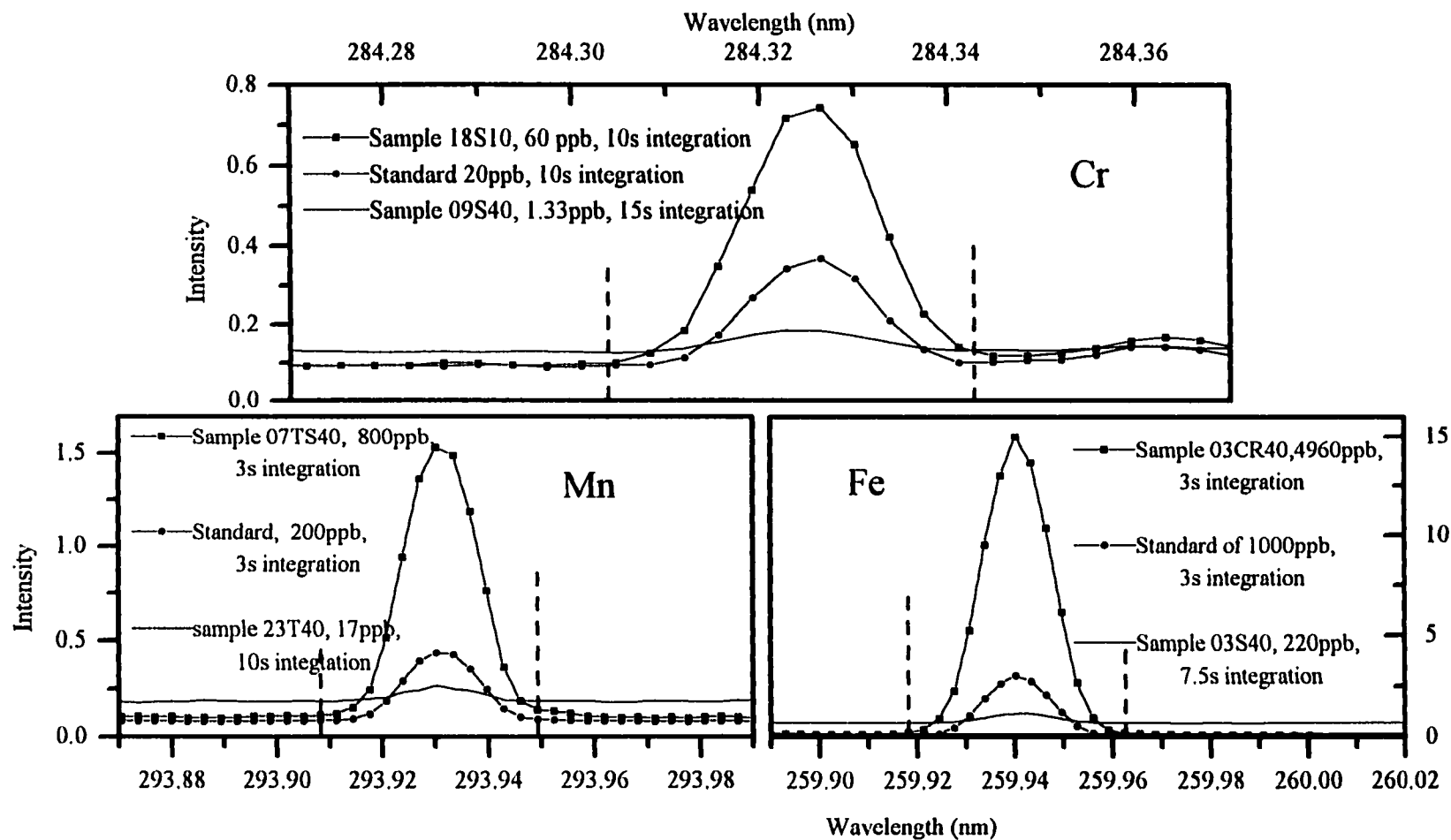


Figure 3.9 Background correction positions for Cr surrounding 284.325nm, Mn surrounding 293.930nm, Fe surrounding 259.940nm.

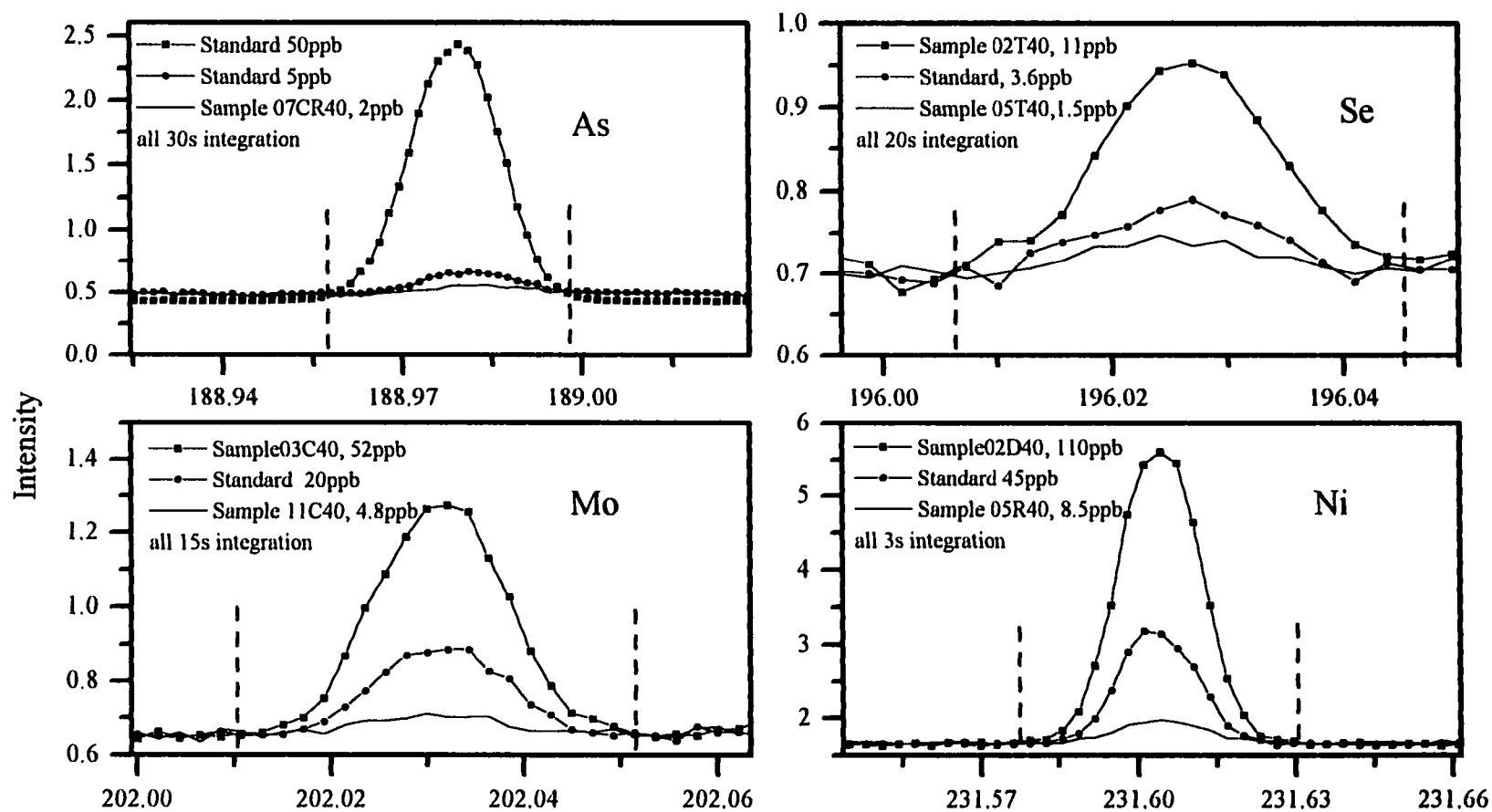


Figure 3.10 Background correction positions for As surrounding 188.979nm, Se surrounding 196.026nm, Mo surrounding 202.030nm, Ni surrounding 231.604nm

All corrections for background are estimates and are therefore subject to uncertainty. In the absence of spectral interferences, the uncertainty is due to noise and, more important, drift in the background. This uncertainty determines the magnitude of the detection limit. In the following section, the factors affecting these uncertainties are further discussed.

3.5 Detection Limit with Integration Time

ICP-AES has been accepted as one of the most promising alternatives to GFAAS and has been used widely for trace elemental analysis in environmental samples [60, 61] such as for sewage sludge and soil analysis [62]. Despite its wide recognition, ICP-AES analyses of complex matrices containing high concentrations of dissolved salts and organic substances require particular care because of the lack of variety of standard reference materials prepared for environmental control. In our sewage leaching experiments, the wide variety of heavy metal components and concentrations is a common phenomenon, and toxic heavy metal concentrations tending to zero is fully expected.

In this work, the ICP-AES technique provided the most precise and accurate results for these complicated matrices. It is the instrumental detection limit (IDL) that plays a critical role for this objective.

Detection limit is generally defined as the minimum concentration of analyte that can be detected at a known confidence level. This limit depends upon the ratio of the magnitude of the analytical signal to the size of the statistical fluctuations in the blank signal. That is, unless the analytical signal is 3 times larger than variations in the blank, with a 99.7% statistical confidence level[42], detection of the analytical signal is not certain. Thus, as the limit of detection is approached, the analytical signal and its standard deviation approach the blank signal S_b and its standard deviation σ_b . The minimum distinguishable analytical signal S_m is then taken to be 3 times the standard deviation of the blank, that is:

$$S_m = S_b + 3\sigma_b \quad (3.3)$$

S_m was estimated experimentally from 11 consecutive integrations of the signal during the continuous nebulization of the blank solution. The resulting data were then treated statistically to obtain S_b and σ_b . In practice, when background correction is applied to the blank spectra, $S_b=0$, equation 3.3 becomes:

$$S_m = 3\sigma_b \quad (3.4)$$

The detection limit depends on both the value of the blank uncertainty and the sensitivity, i.e. the slope of the calibration line in Figure 3.11.

$$C = mS + b \quad (3.5)$$

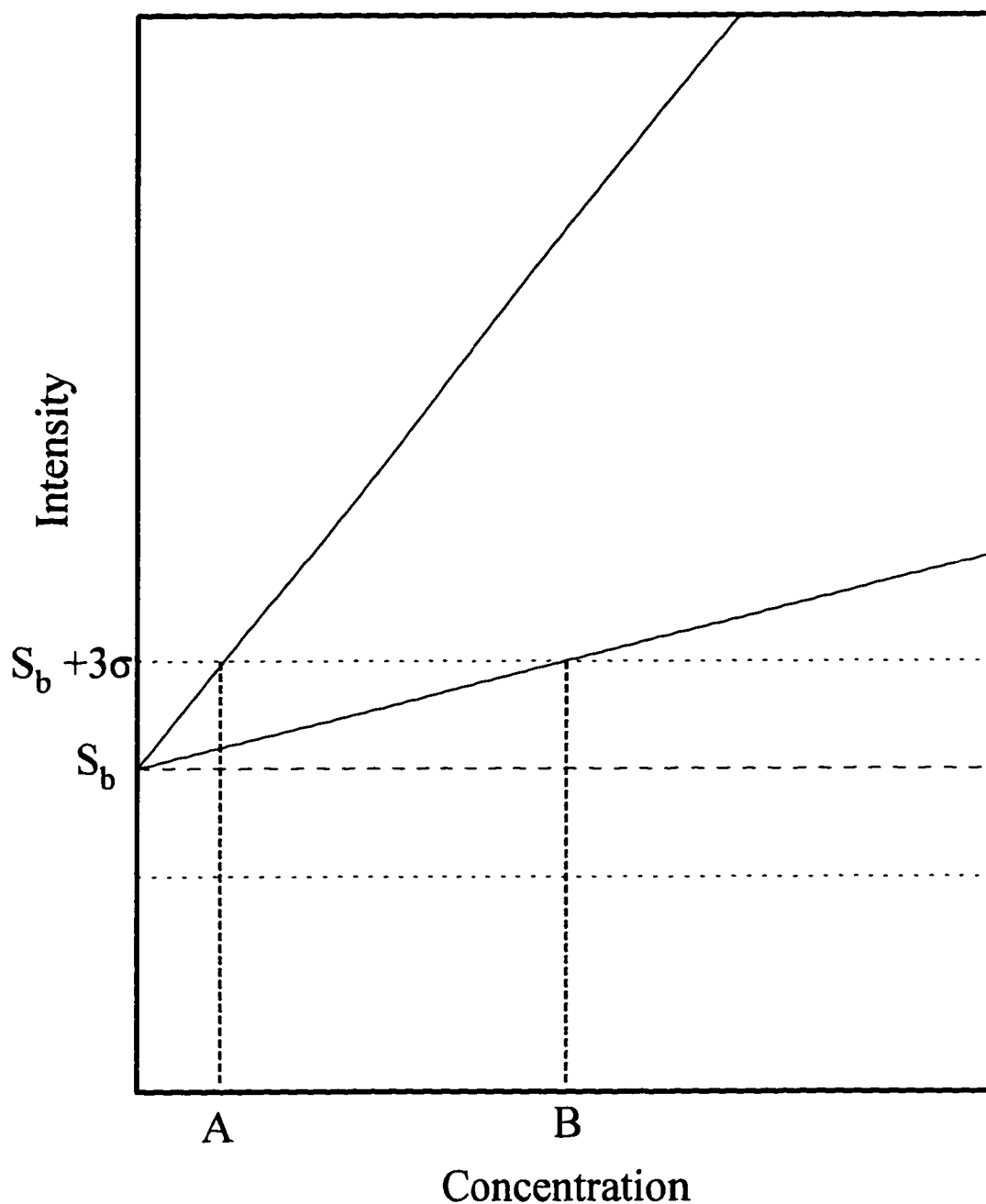


Figure 3.11 The determination limit refers to the concentration at which the analyte signal intensity is equal to the mean blank signal (S_b) plus three times the standard deviation σ of a blank. For the same x and σ , a line of higher sensitivity (slope) will have a lower detection limit (A) than that of a less sensitivity line (B)

Finally, the minimum distinguishable analytical signal S_m in equation 3.3 is inserted into equation 3.5 to obtain the detection limit D_L in concentration units.

$$D_L = 3m\sigma_b + b \quad (3.6)$$

However, D_L is still related to the analyte calibration sensitivity m in equation 3.6. For a standard with concentration C_s high enough to give a confidently detectable signal S_s ,

$$m = \frac{C_s - b}{S_s} \quad (3.7)$$

Combining equations 3.7 and 3.6, we obtain:

$$D_L = 3(C_s - b)\sigma_b / S_s + b \quad (3.8)$$

Instrumental factors that increase the sensitivity without affecting background noise improve the instrumental detection limit (IDL). Both sensitivity and blank noise level depend on the length of time over which the stabilized signal from the ICP is integrated. The sensitivity is proportional to the integration time,

$$S_s = a_1 t \quad (3.9)$$

where a_1 is proportionality constant.

Since noise is random and has a "white" spectrum, the standard deviation of the blank noise should vary as the square root of the integration time,

$$\sigma_b = a_2 \sqrt{t} \quad (3.10)$$

Combining equation 3.9, 3.10 into equation 3.8, the relationship between IDL and analyte integration time t is

$$D_L = 3(C_s - b) \frac{a_2}{a_1} \frac{1}{\sqrt{t}} + b = \frac{d}{\sqrt{t}} + b \quad (3.11)$$

where $d = 3(C_s - b)a_2/a_1$

Therefore D_L can be improved by increasing the instrumental integration time. The limited data available suggest that this relationship is true for integration times in the normal range 1 to 30s. Figure 3.12 shows how D_L varies with $1/\sqrt{t}$ for Cu at 254.754nm using the instrumental conditions listed in Table 3.1. In Figure 3.12, the first part of the data curve is fitted well to equation 3.9, but for integration times longer than 10 s, the D_L increases. This clearly tells us that a modest increase in integration time can improve the detection limit. For prolonged integration times, the relationship between detection limit and integration time in equation 3.11 is obviously invalid, because factors other than instrumental noise come into play. Figures 3.14 and 3.15 illustrate that the background signal varies both randomly and systematically within the period between calibration points. The shorter integration times used for IDL estimation are spaced very closely in time and represent a minimum possible variance that is dependent most on random errors. Integrations over a longer period show a larger variance because systematic drift and correction errors dominate the DL [63]. Therefore a best integration time exists giving the lowest detection limit before instrumental drift deteriorates the signal (Point A in Fig 3.13). We call this detection limit the "Absolute" Instrumental Detection Limit

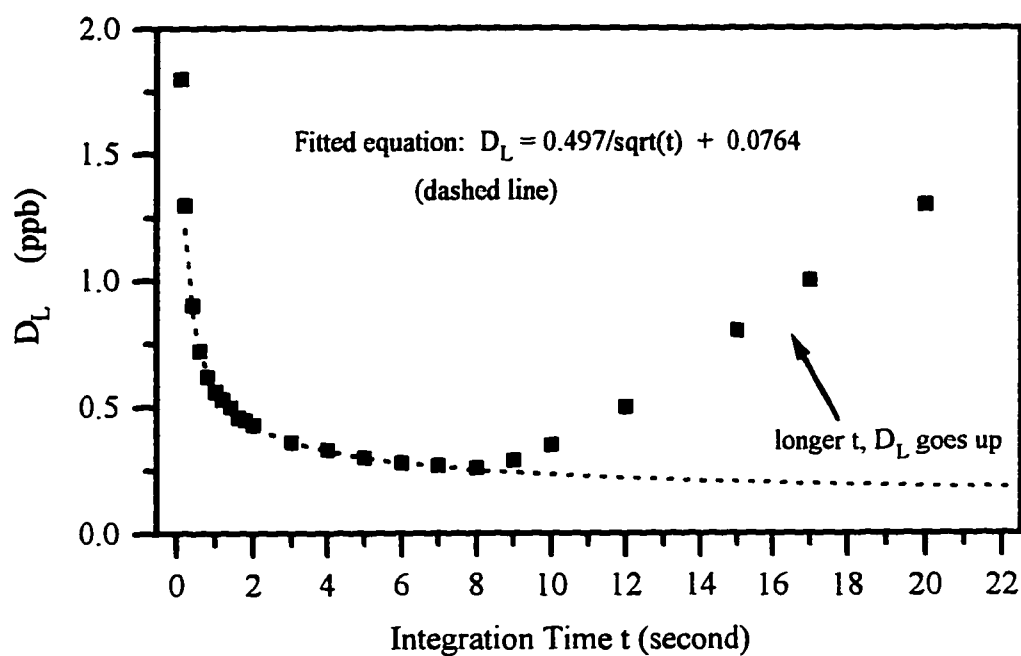


Figure 3.12 Detection Limit with Integration Time for Cu at 324.754nm.
The dashed line is fitted to equation (3.9).

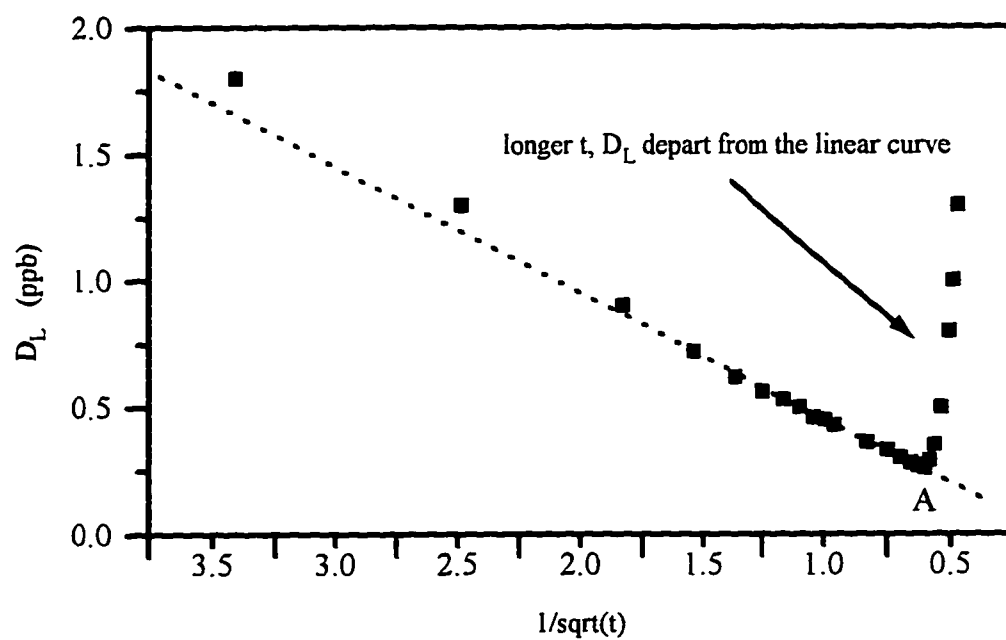


Figure 3.13 Detection Limit with Reciprocal of Square Root of Integration Time
for Cu at 324.754nm, dashed line is equation (3.9) fitted.

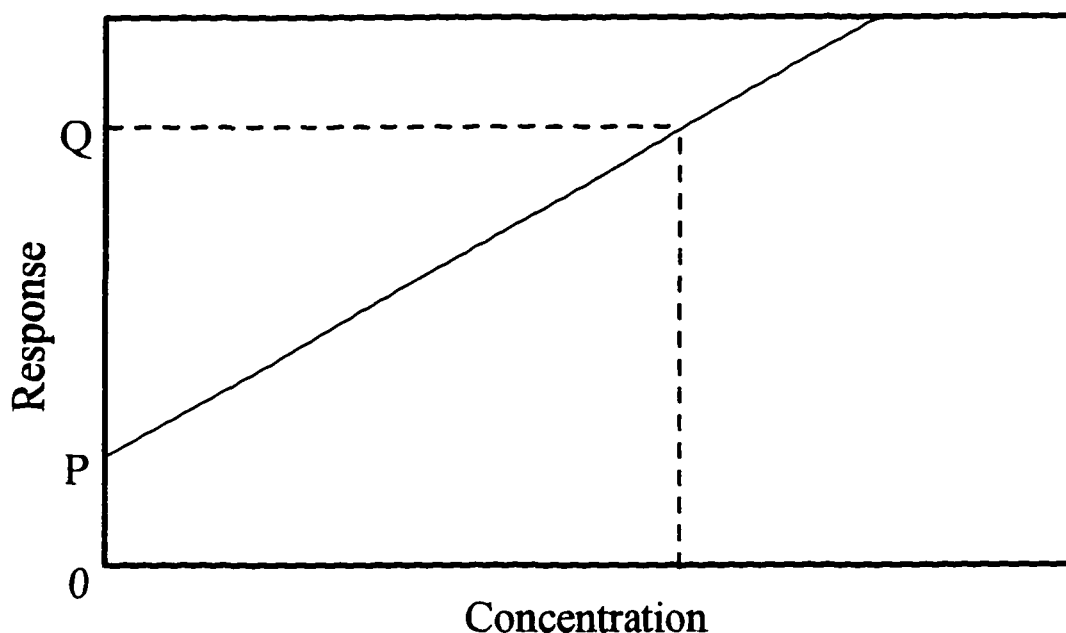


Figure 3.14 A schematic calibration with two fixed points P and Q

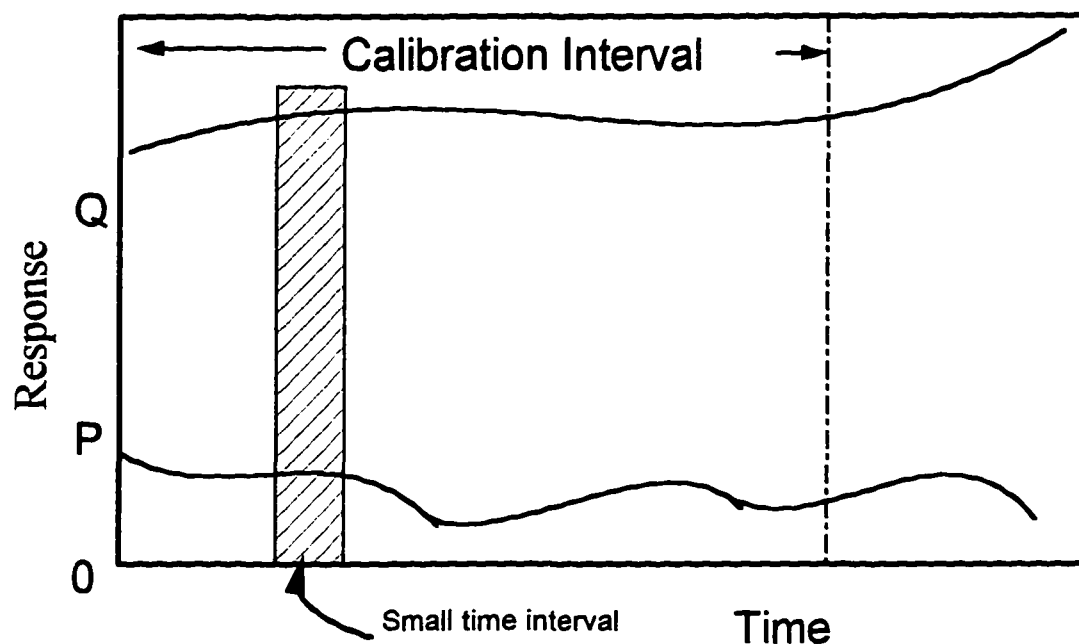


Figure 3.15 Variation in the position of P and Q on the response axis with the passage of time, showing exaggerated drifts. The SD of a number of measurements of P and Q repeated within a small time interval would be much smaller than a SD of results scattered within the calibration intervals. Precision and DL usually cited refer to the small interval.

(AIDL) in our study to represent the lowest IDL for the analyte line, because the IDL varies with integration times. In Table 3.3 are also listed the detection limits for the selected integration time used for each element in the leachates.

In order to match the trace heavy metal concentration in leachates, the lowest concentration of the standard for each element was 5 times of AIDL.

3.6 Standard Deviations with Detection Limit

As shown in Figure 3.13, although a minimum integration time with a sound detection limit can provide a fast analysis in this sequential line instrument, this integration setting may not represent the optimum instrument condition for leachate solutions. As seen in equation 3.1, for the best match of blank and standard matrix, the detection limit is only related to the standard deviation of a blank [64]. In fact, the deviation of the analyte determinations not only affects the precision and accuracy of the results, but also in turn affects the detection limit in samples. Therefore, the correlation of the variation in analyte signal determination with instrument integration time is necessary for optimizing analysis conditions.

In ICP the noise typically takes the form of the time variation of the signal about the mean [63]. Therefore, the noise N is conveniently defined as the standard deviation of the signal while the signal S is given

by the mean. The relative standard deviation (RSD) is then the reciprocal of the signal to noise ratio, that is

$$RSD = \frac{s.d.}{mean} = \frac{N}{S} = \frac{1}{S/N} \quad (3.10)$$

where s.d. is standard deviation.

As discussed in the previous section, S/N is proportional to the square root of total integrating time. RSD is ultimately inversely proportional to the integration time,

$$RSD = \frac{a}{\sqrt{t}} \quad (3.11)$$

In this experiment, 11 replicates of the following solutions were run with different integration times for each interest analyte line.

- 1). one leachate sample with concentration close to 5 times of the AIDL of analyte of interest.
- 2). one leachate sample with mid-concentration of the analyte of interest.
- 3). one standard with concentration close to 5 times of AIDL of analyte.
- 4). one standard with mid-concentration of analyte.
- 5). one standard solutions at highest concentration of analyte.

Figure 3.16 and 3.17 illustrate the RSD relationship with integration time for Cu at 324.754nm. Again by analogy to D_L with lower t , the experimental data have a linear relation with $\frac{1}{\sqrt{t}}$, as predicted by equation 3.11. With the longer integration time, RSD degrades similar to D_L . However, when integration time is extremely short, RSD data for low concentrations in both sample and standard

depart from the linear curve (Figure 3.17). But this is not observed in the relationship between D_L and t for low integration times (Figure 3.13). This can be explained by a careful examination of equations 3.8 and 3.10. When the analyte concentration is as low as the blank, $s.d.$ and σ_b are comparable at the same integration times. However, trace concentrations using short integration times are essentially undetectable; hence the uncertainty in determining the "mean" in equation 3.10 is higher, and hence the uncertainty in determining RSD is higher. Therefore equation 3.10 is invalid at low integration with low concentration of sample. The signal S_s in equation 3.8 can be determined with much higher certainty when a higher concentration standard is used.

It is also worth noting from Figures 3.16 and 3.17 that the RSD is strongly concentration-dependent, and the higher concentrations of the analyte give better RSD's. That means that a shorter integration time is sufficient to achieve a certain RSD, compared with samples with the lower concentration levels. Therefore it can be concluded that the standard addition method may give better analytical precision and accuracy.

Figure 3.18 shows the relationship of D_L and RSD to t for the lowest sample concentration with integration time t for the Cu line at 324.754nm. From these graphs, the minimum integration time with best values for both D_L and RSD was selected for each element. Therefore the best integration time can be selected between 4s and 8s in Figure 3.18. In Table 3.3 are listed the integration times selected in this way

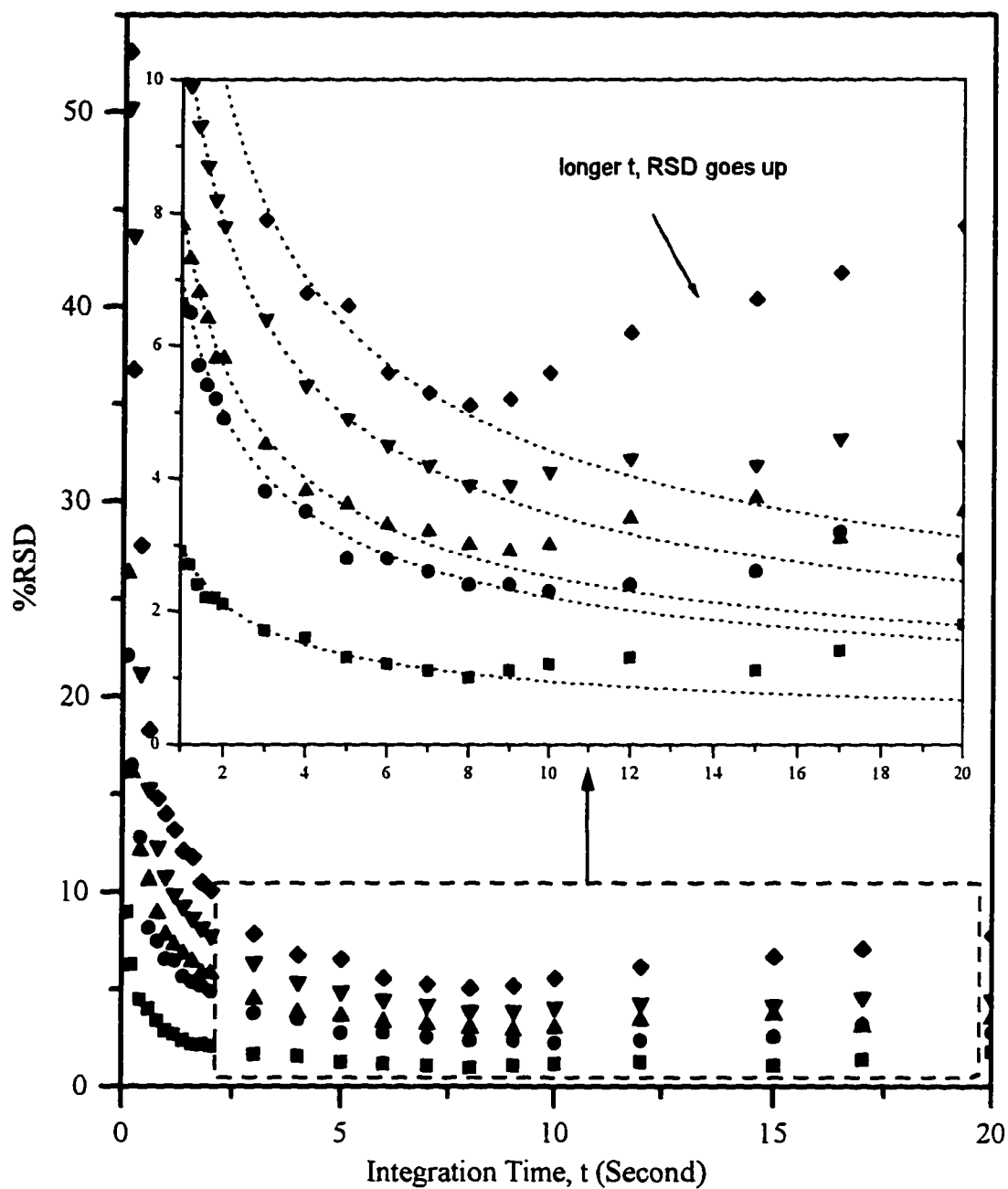


Figure 3.16 %RSD with Integration Time t at 254.754nm for Cu standards and Samples.

- Standard, 400ppb ● Standard, 100ppb ▲ sample 01R40, 120ppb
 ▼ Standard, 2ppb ◆ sample 15R40, 2.5ppb
 dashed lines are fitted using equation (3.11).

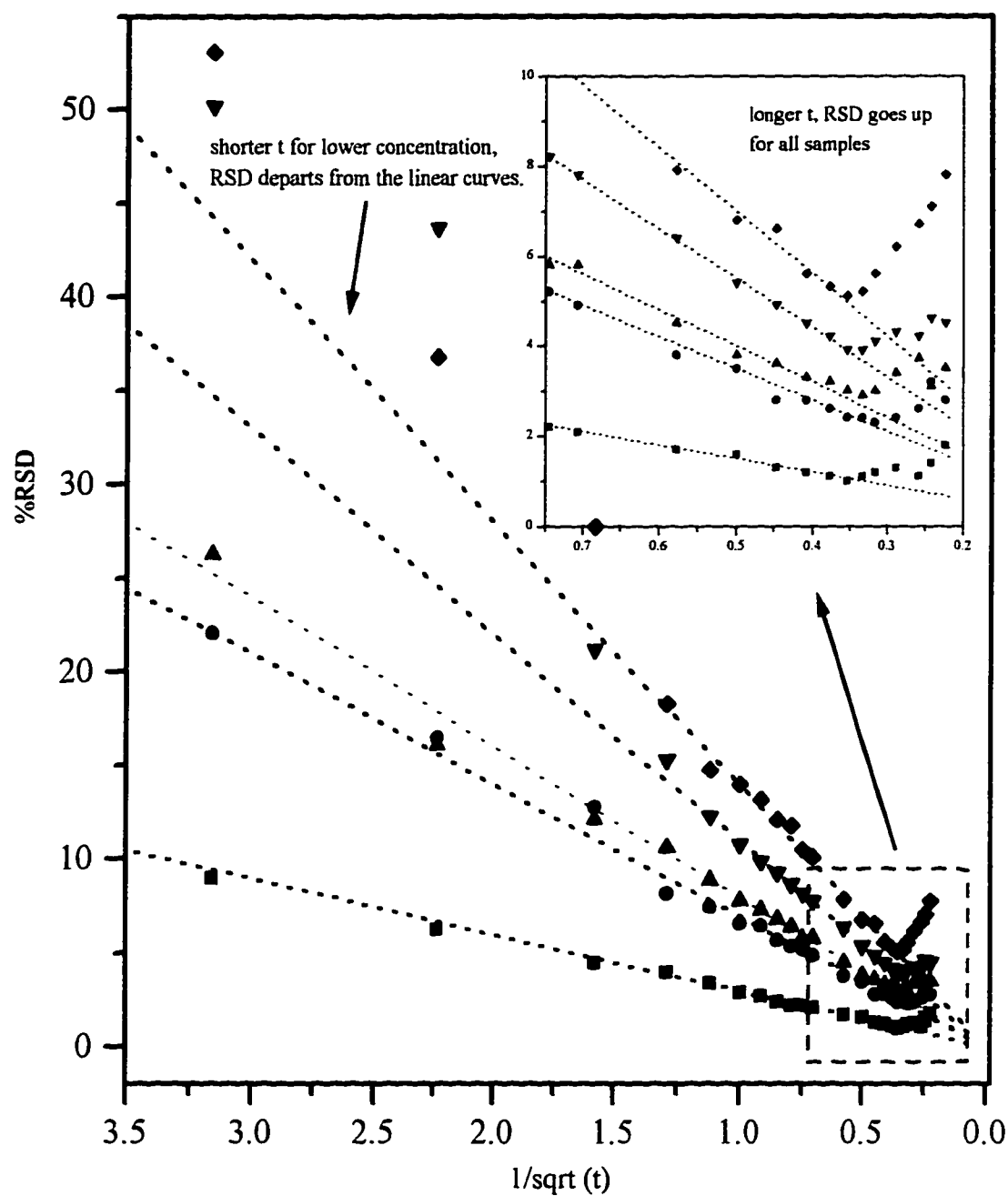


Figure 3.17 %RSD with Reciprocal Square Root of Integration Time.

- Standard, 400ppb ● Standard, 100ppb ▲ sample 01R40, 120ppb
 ▼ Standard, 2ppb ◆ sample 15R40, 2.5ppb
 dashed lines are fitted using equation (3.11).

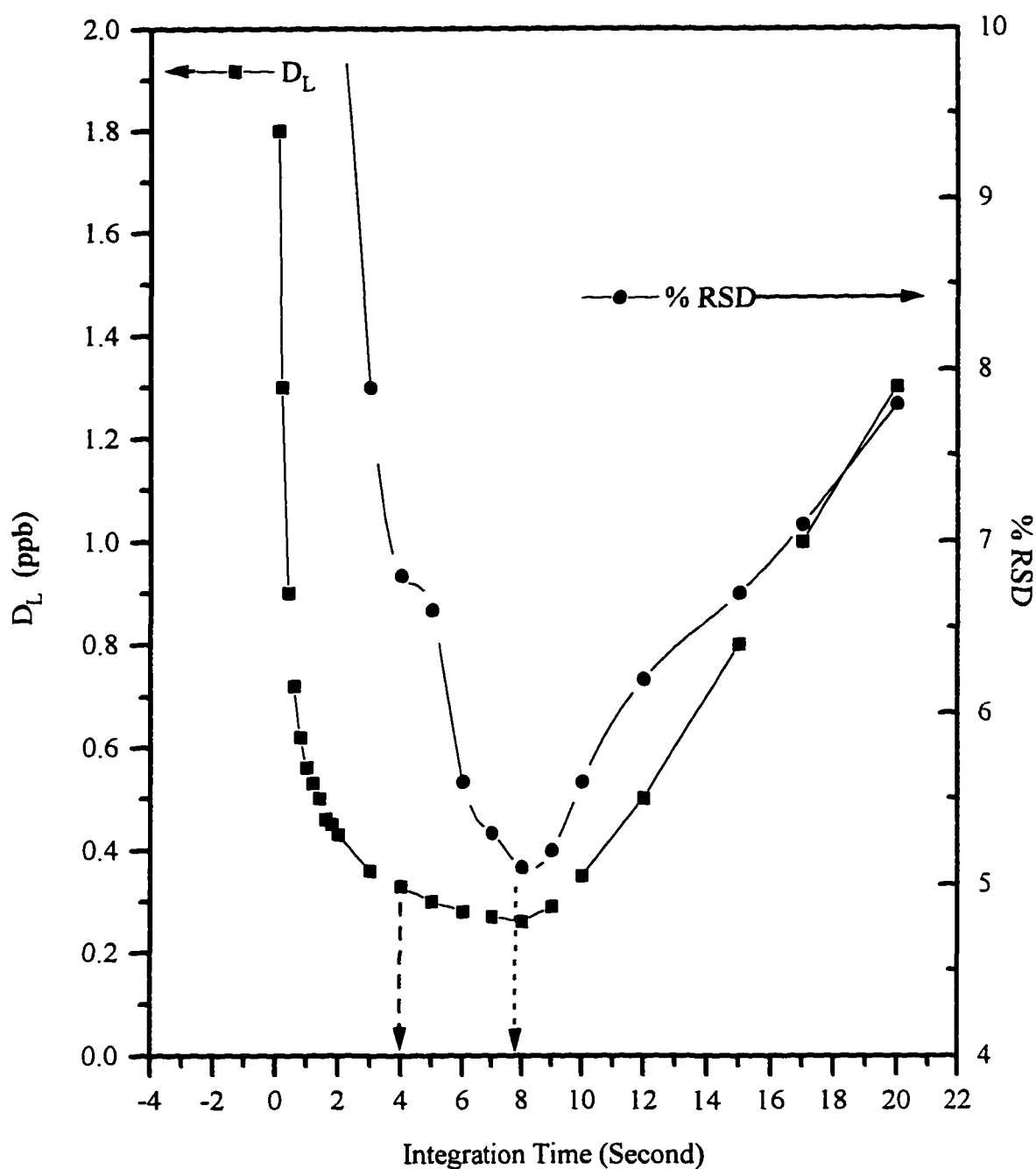


Figure 3.18 Graphical Overlays of Detection Limit and % RSD with Integration Time for Cu at 324.754 nm, 6s was selected between the minimums of D_L and %RSD

—●— %RSD is obtained with sample 15R40, 2.5ppb

for each analyte line used to analyze the leachate samples and its corresponding DL. The DL is not same as the AIDL for most analyte lines discussed in Section 3.4.

3.7 Spectral Purity and Signal to Noise Ratio

If other analyte lines and matrix signals exist in the vicinity of the spectra of interest from one sample, they may not be distinguishable if their intensities are not high enough over the background. However, these interfering lines may take on significance in some samples. Therefore it becomes important to evaluate how the matrix and noise affect the signal in the vicinity of the analyte line of interest. So far no literature has been found evaluating spectral purity in ICP-AES, although there are a few studies on noise characteristics of ICP [65-68]. In this thesis, the spectral data narrowly close to the analyte line are processed mathematically by a Fourier Transform method to elucidate the information on spectral purity. Conventionally, the Fourier Transform technique is applied to the time domain data acquired with assistance of an interferometer such as in FTIR spectrometry. The frequency domain spectrum is the final result [69]. However in this paper, the intensities of the selected range of spectra were treated as one full cycle of the interferogram, and the frequency of intensity variation in this data cycle was derived using a Fourier Transfer method. The software used here is Origin mathematics data analysis version 2.8.

Figure 3.19 shows the spectra of Cu surrounding 324.754 nm at 3 different integration times. Figure 3.20 illustrates the frequency domain plots transferred from the three spectra of Cu over the wavelength range from 324.5987 nm to 324.8398 nm using different integration times. 152 data points in the spectral range were used as one cycle of the interferogram. This intensity vs. frequency plot consists of 3 parts. The first part, with high intensity and frequency between 0 and 4, contributes the main portion of the analyte peak at 324.775 nm in the spectra. The second part of the plot, approximately between frequency 4 and 60, represents most of the matrix signals or background signal. However, the high frequency part with low intensity comes from the instrumental noise. The higher intensity at lower frequencies indicates the smaller variation of the spectral peak intensity, and higher intensity in higher frequencies indicates both the higher variation of the peak intensity and the higher background intensity.

Figure 3.21 shows the first and second parts from Figure 3.20 in which the intensity data for 3 integration times are proportional to their corresponding peak and background intensities shown in Figure 3.19. Thus, when the intensity plot with 0.1s integration is multiplied by 10, and that with 0.5s is multiplied by 2 in Figure 3.21, the overlap of the plots with 1s integration in Figure 3.22 indicate again that the signal increase is directly proportional to the integration time, and the matrix has a similar integration time relationship as the analyte signal.

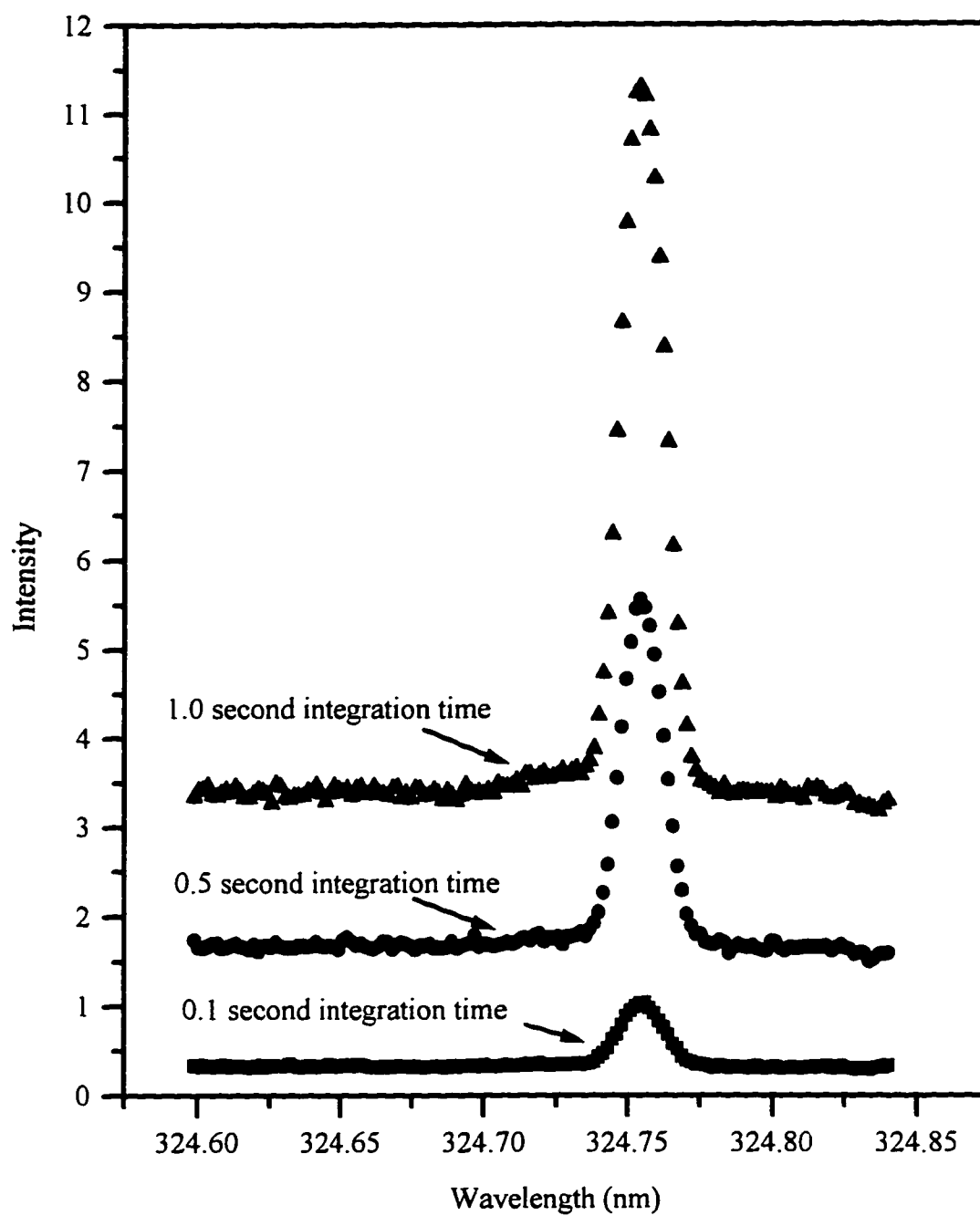


Figure 3.19 Spectra of 500ppb Cu standard solution surrounding 324.754 nm at 3 different integration times.

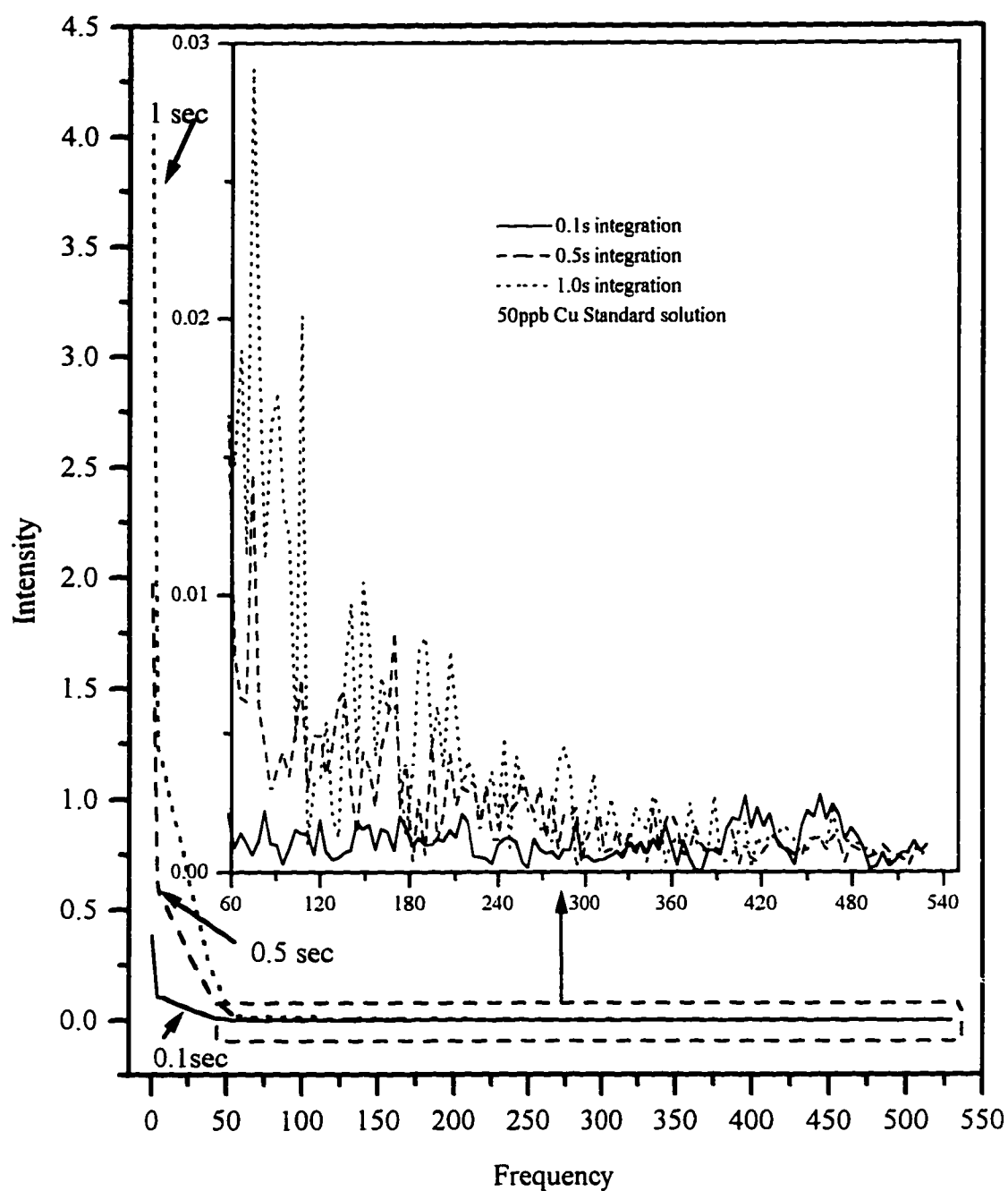


Figure 3.20 Data Variance of Spectra in Figure 3.19. The frequency domain plots are obtained by Fourier Transform of Spectra in Figure 3.19, where all the data are treated as a full cycle.

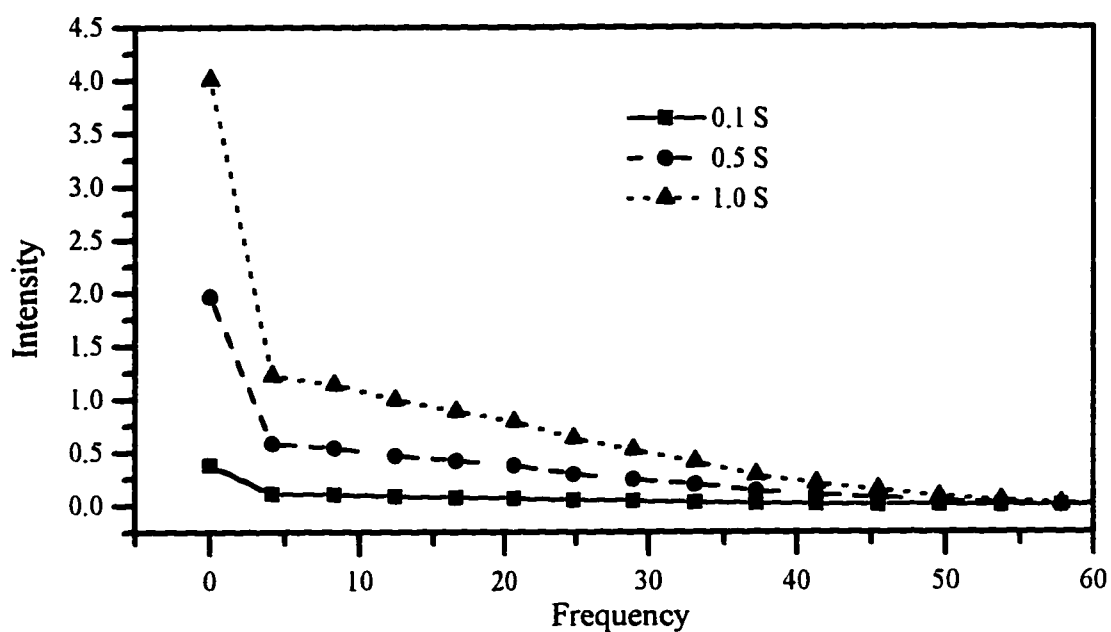


Figure 3.21 Frequency Domain Plots of Signal and Matrix Parts in Figure 3.20, 50ppb Cu Standard Solution.

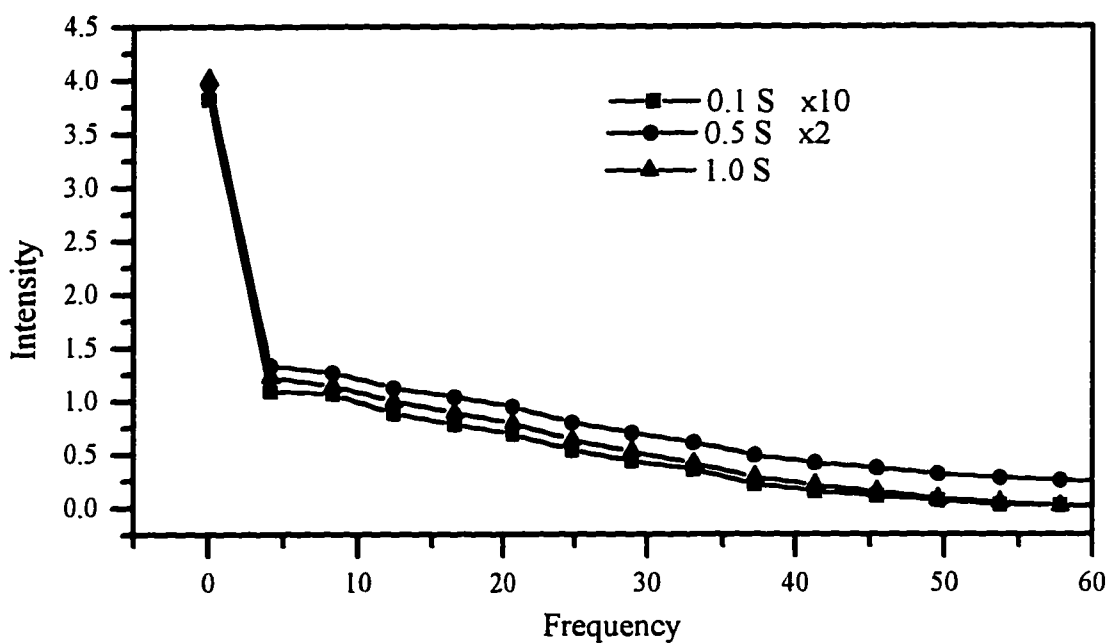


Figure 3.22 Intensities in Frequency Domain Plots of with 0.5s Integration multiplied by 2, and that with 0.1s by 10 in order to match up with the intensity with 1s integration signal. The three plots coincide completely.

The noise part of Figure 3.20 is shown in Figure 3.23. Figure 3.24 shows the modified part of Figure 3.20, in which the intensity data for 0.1s integration are multiplied by $\sqrt{10}$, and that for 0.5s integration multiplied by $\sqrt{2}$. Though the overlap of the three plots in Figure 3.24 is not as perfect as in Figure 3.22 for analyte and matrix signals because of the properties of noise itself, the overlap is much better than in Figure 3.23. This indicates that the noise increase is approximately proportional to the square root of the integration time in this integration time range.

Figure 3.25 shows the spectral comparison of the same 50 ppb concentration of standard and sample solutions. After Fourier transformation in Figure 3.27, the better quality of the spectra from the standard solution, with higher intensity at low frequencies and lower background intensity at higher frequencies, are distinguishable from those of the sample solution.

Furthermore, spectra scanned near 327.396 nm and 324.754 nm are also compared in Figure 3.26. The frequency domain of the plots in Figure 3.27 indicates higher intensity at higher frequencies for Cu at 327.396 nm line, which implies a higher variation in spectral peak and background intensity. When instrumental noise shows a similar pattern for sample and standard at same analyte line for Cu (Figure 3.29), however, spectral data surrounding 327.396 nm in Figure 3.28 show obviously higher frequency noise than the data surrounding 324.754 nm.

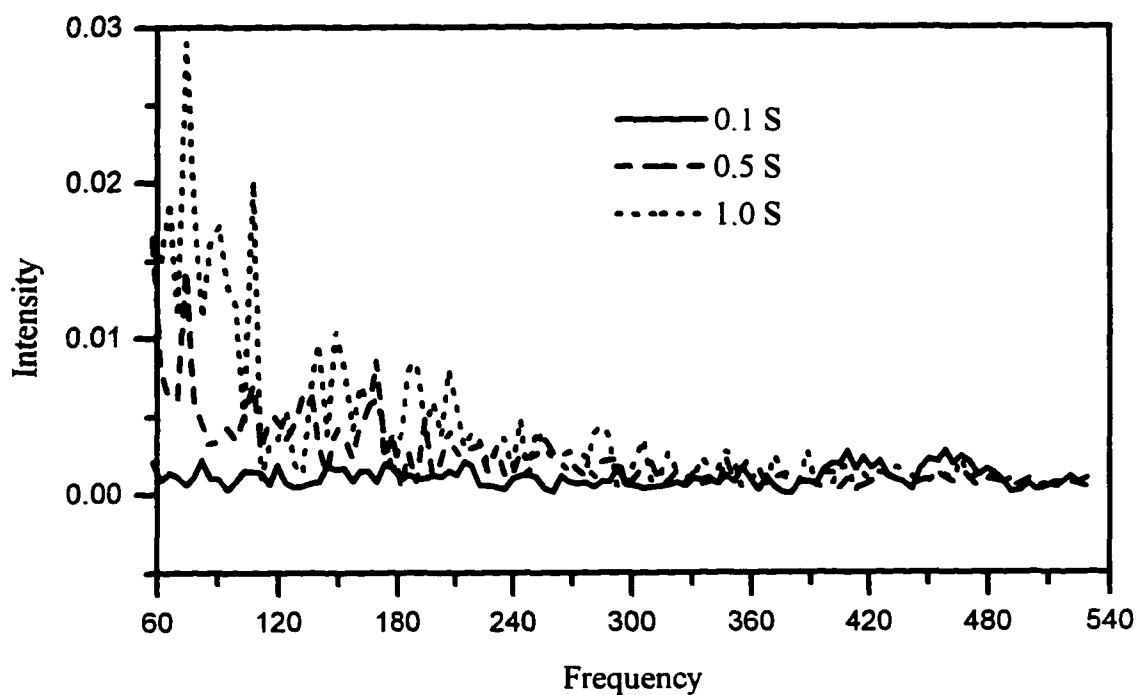


Figure 3.23 Frequency Domain Plots of Noise Parts in Figure 3.20

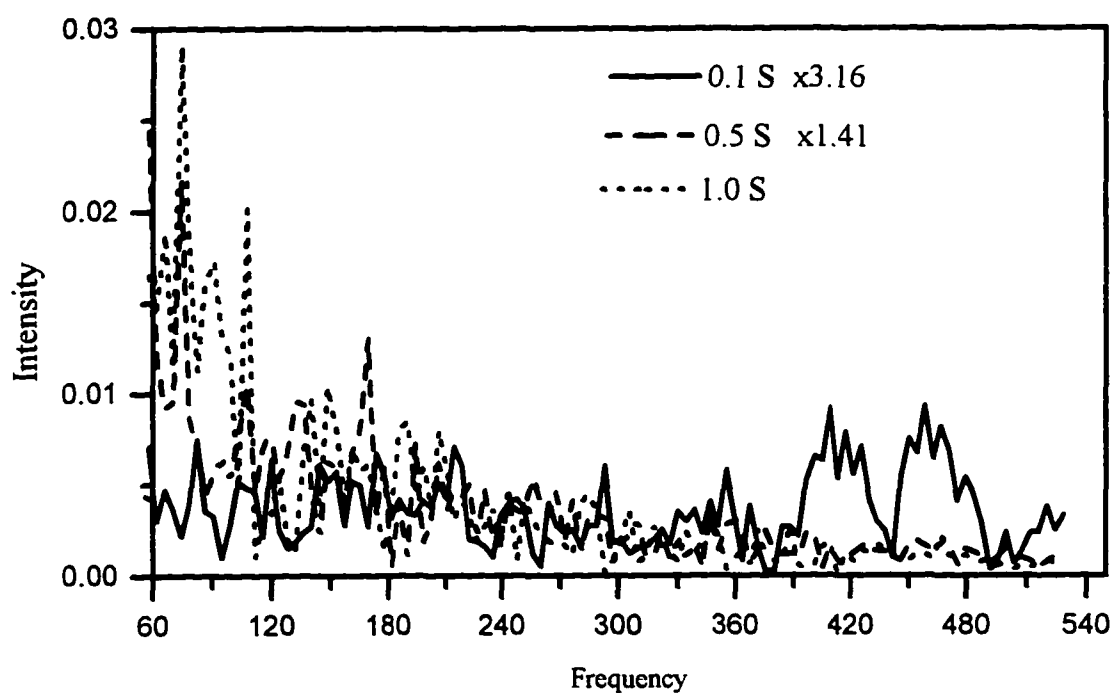


Figure 3.24 Intensities in Frequency Domain Plots of Noise Part in Figure 3.20 with 0.5s integration multiplied by 1.41, and that with 0.1s by 3.16 in order to match up with the noise intensity with 1s integration. The three plots coincide much better than in Figure 3.23.

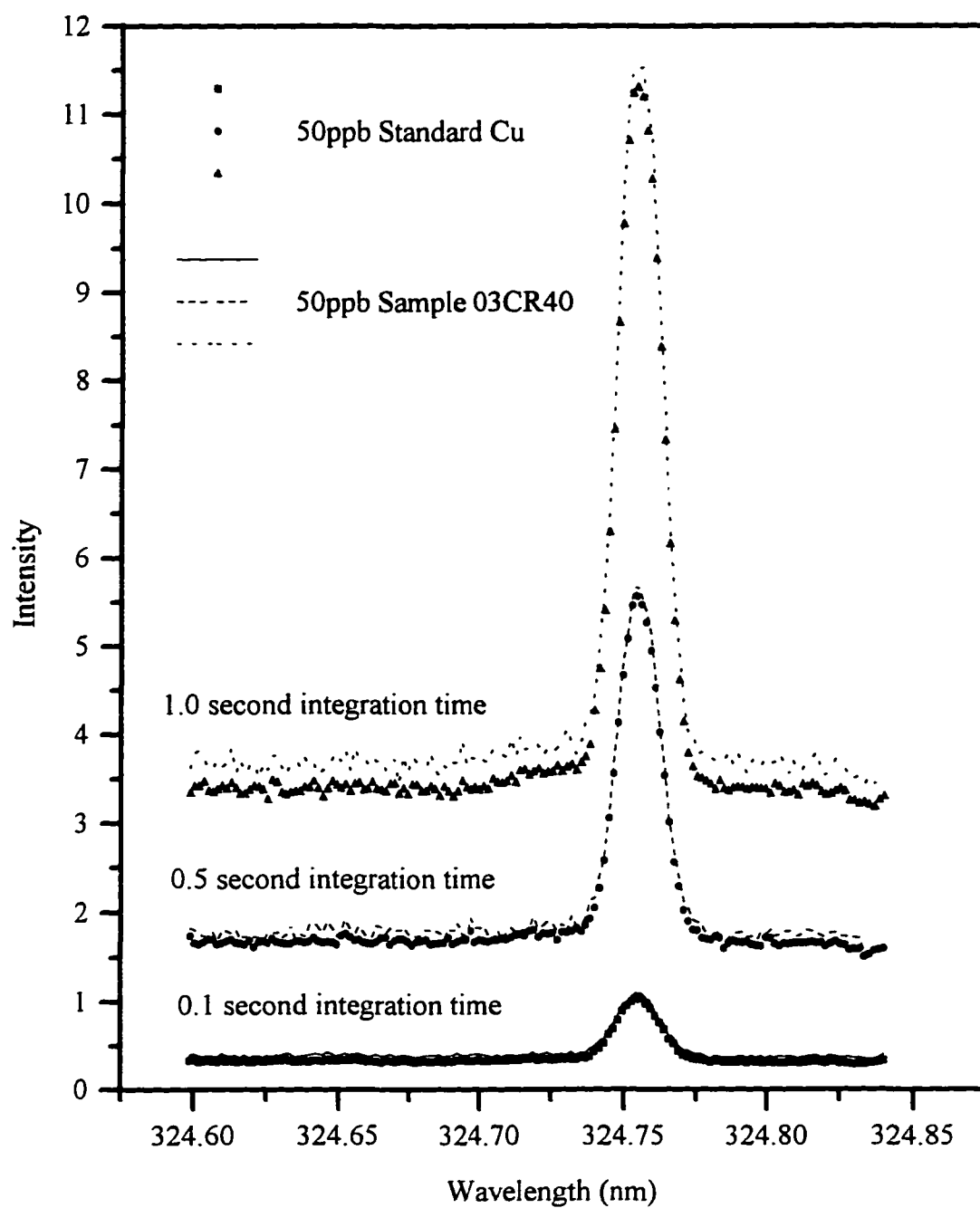


Figure 3.25 Spectral comparison of Cu standard and sample 03Cr40 at same concentration (50 ppb) surrounding 324.754 nm with different integration times.

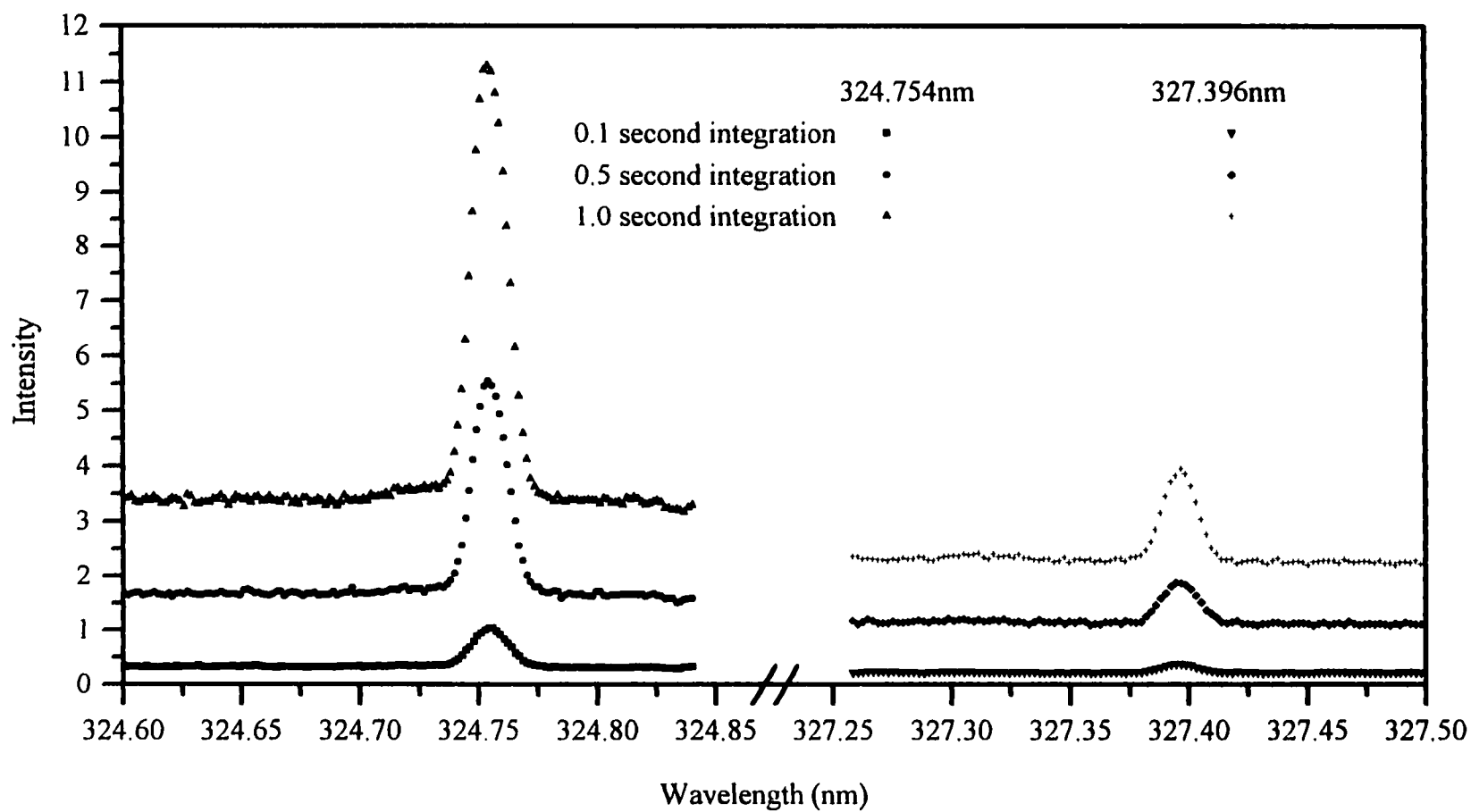


Figure 3.26 Spectra of 50ppb Cu standard solutions scanned surrounding 324.754 nm and 327.396 nm

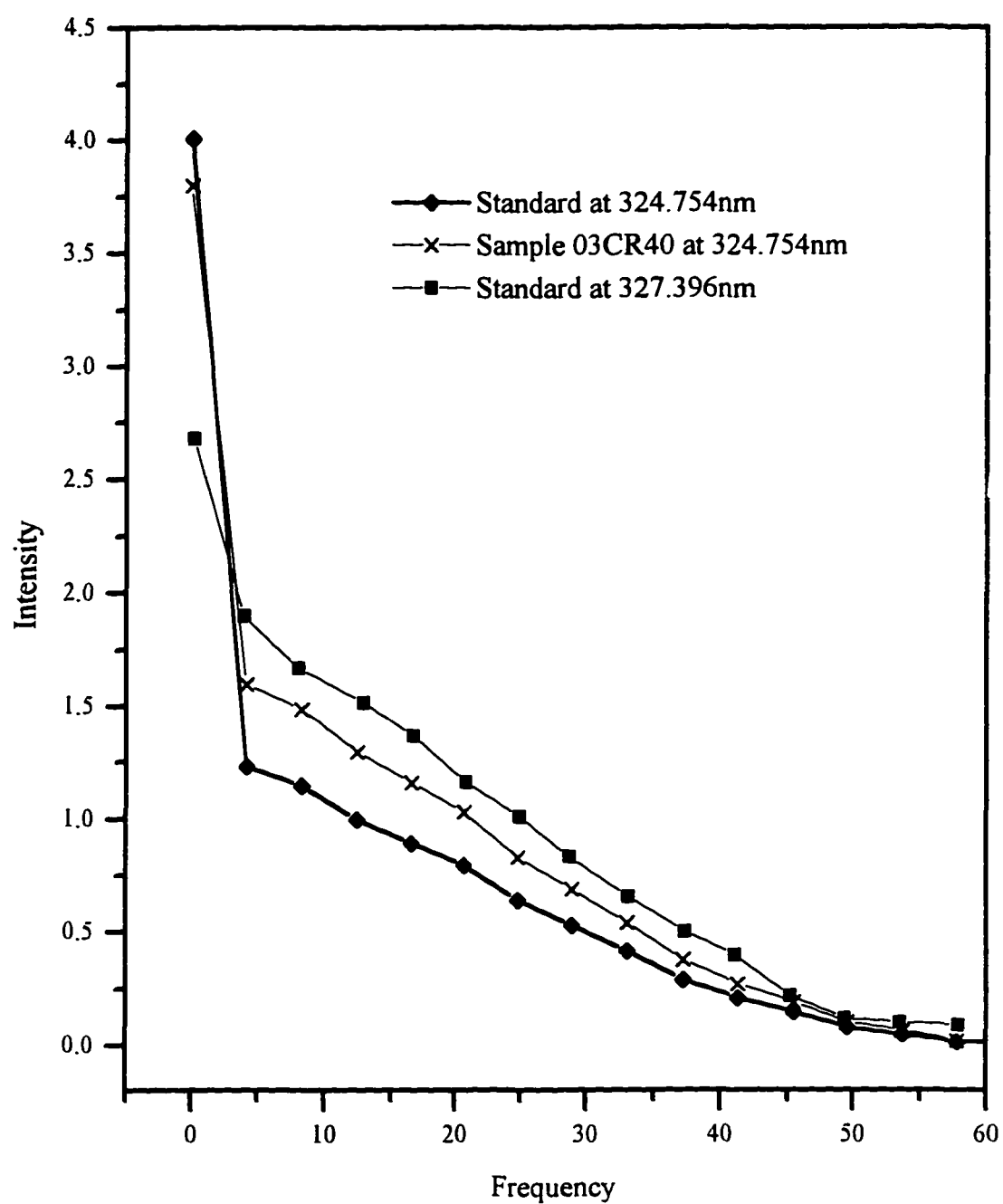


Figure3.27 Frequency domain plots of Cu spectral data at 324.754 nm with standard and sample 03CR40, and at 327.396 nm with standard, all concentrations 50 ppb, 1s integration.

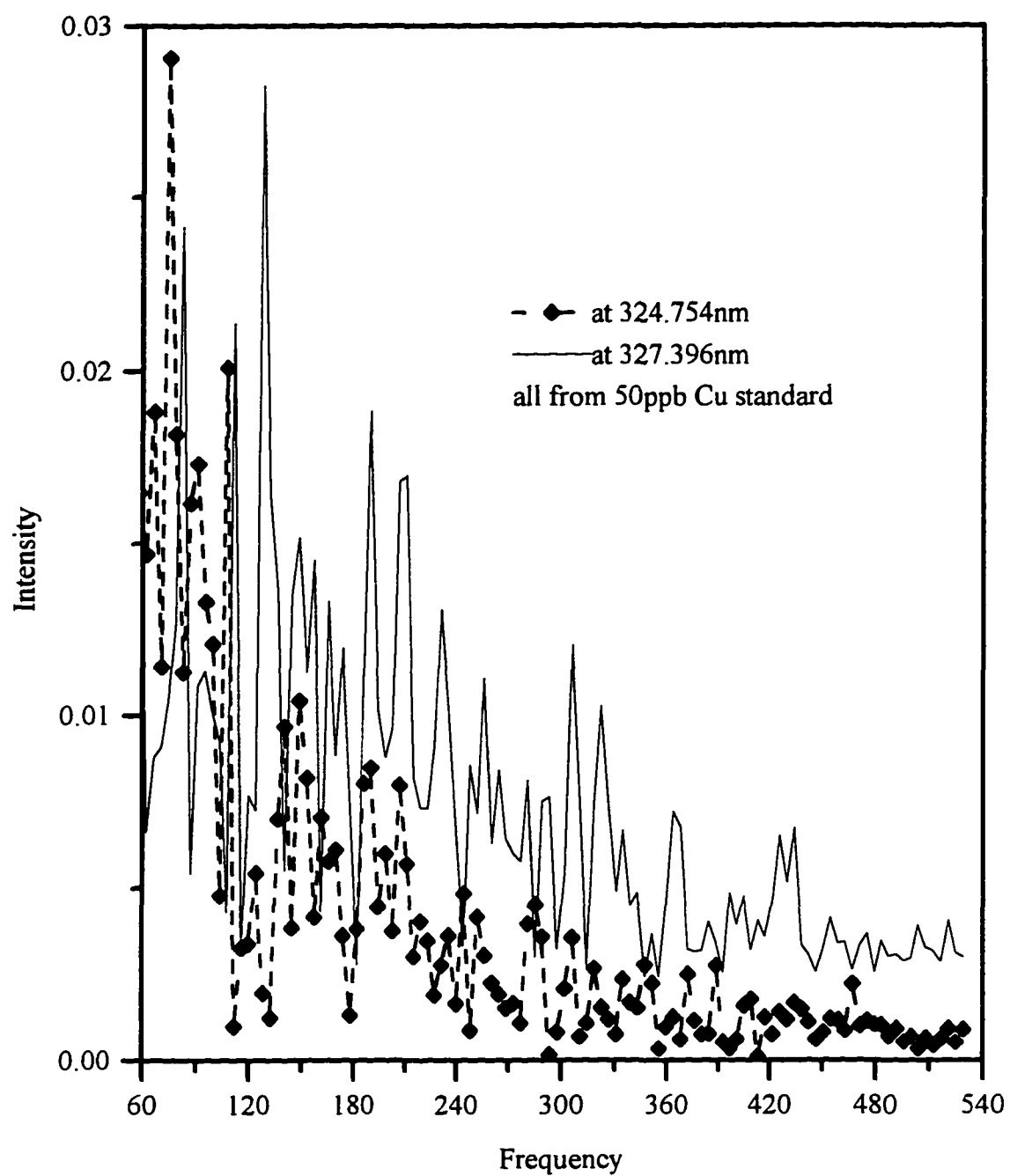


Figure 3.28 The overlap of the instrumental noise in spectra for 50ppb Cu standard solution surrounding 324.754nm and 327.396nm, 1s integration.

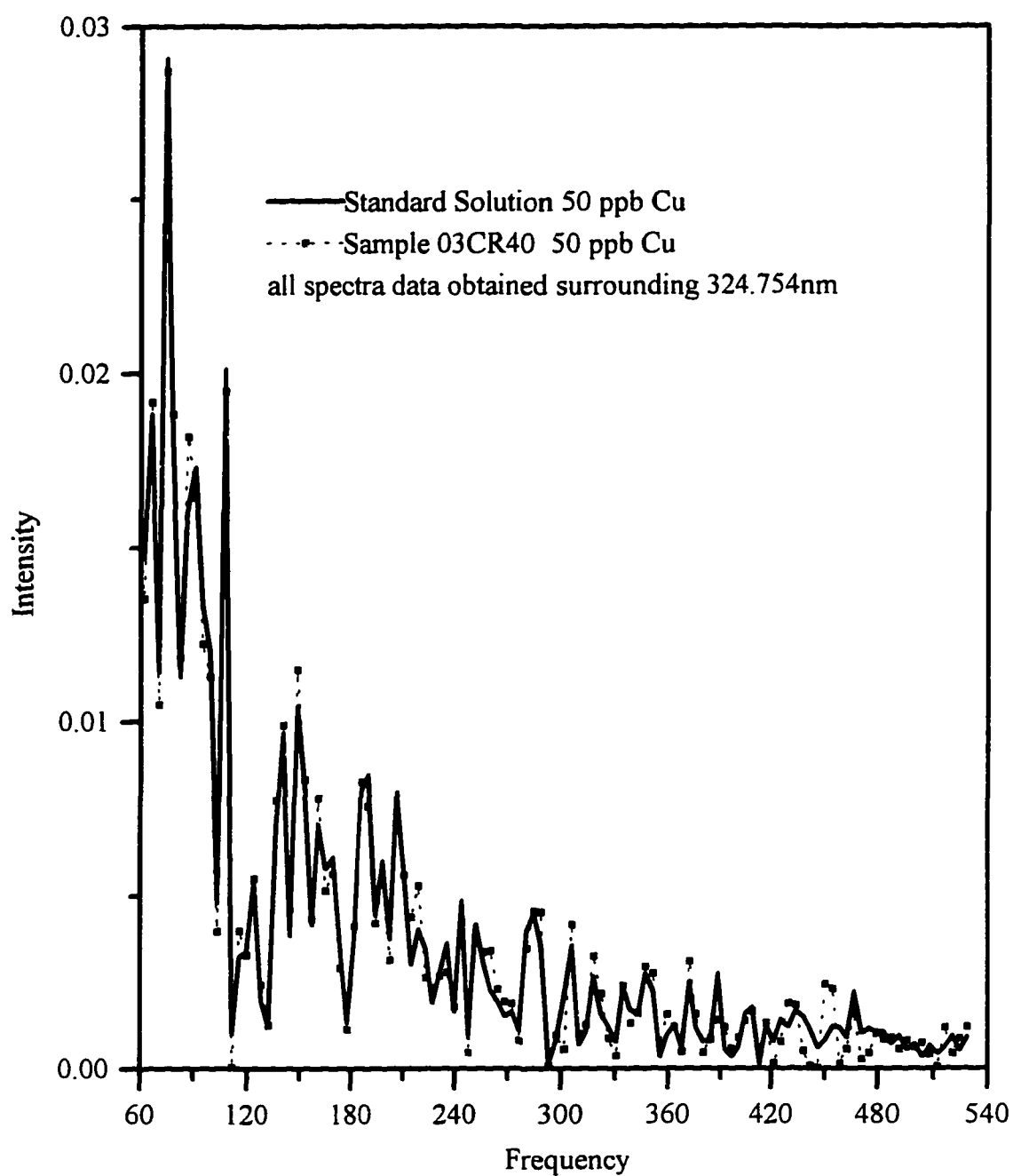


Figure 3.29 The overlap of frequency domain plots for instrumental noise from spectral data surrounding 324.754nm, using 50ppb Cu standard solution and sample 03CR40, at 1s integration.

Compared with the evaluation of signal to noise ratio in Section 3.6 using the standard deviation of replicate determinations of a individual analyte line, the Fourier Transfer data processing method provides a comprehensive analysis of signal to noise for a range of data over the spectrum. In this research, the Fourier transfer method, combined with other criteria discussed in previous sections, was used to help select analyte lines listed in Table 3.3.

3.8 Internal Standardization Method

Although a sample introduction system in conjunction with ultrasonic nebulization (USN) for ICP-AES has attracted attention [70-72], there have been only a few reports concerning the application of USN in sewage and soil studies. The detection limits of ICP-AES with USN are reported to be at least one order of magnitude lower than those obtained by ICP-AES. However, because matrix interferences encountered in ICP-AES are normally associated with the surface tension, viscosity and dissolved solids content of the samples, it has been pointed out that the use of the USN causes a poorer precision [73]. Any difference in properties between the samples and standards may cause erroneously high or low results due to nebulizer uptake rate or sample aerosol transport. In order to overcome these disadvantages of USN, an internal standardization was used in this study to overcome

these potential interferences, and the method developed was applied to the determination of trace elements in leachate solutions.

As a general rule, an element used as an internal standard must have the following properties:

- 1). behavior similar to the analyte in the plasma, such as increase in signal with increase in power.
- 2). same concentration in all calibration standards, the blank, and unknown samples.
- 3). simple spectrum so that no spectral interference are created by adding internal standard element.
- 4). chemically compatible with the sample, e.g. no precipitate formed by reaction of sample with the internal standard element.

Yttrium, which is often used as an internal standard, in environmental soil and sludge studies in ICP-AES [74,75], was also selected for this research. Before yttrium was added to any sample, representative samples of each type of sewage and soil studied, in which the concentrations of elements of interest were 100 times higher than in leachate solutions, were scanned against each prominent yttrium line listed in Table 3.3. This procedure was employed to ensure that there was no yttrium originally in any leachate samples. The spectra scanned near 378.870 nm on 6 digested samples with 10s integration (Figure 3.30) indicated that there is no Y signal observed in these samples, for comparison, the spectra of a 1ppm Y standard with 3s integration was incorporated into each spectrum.

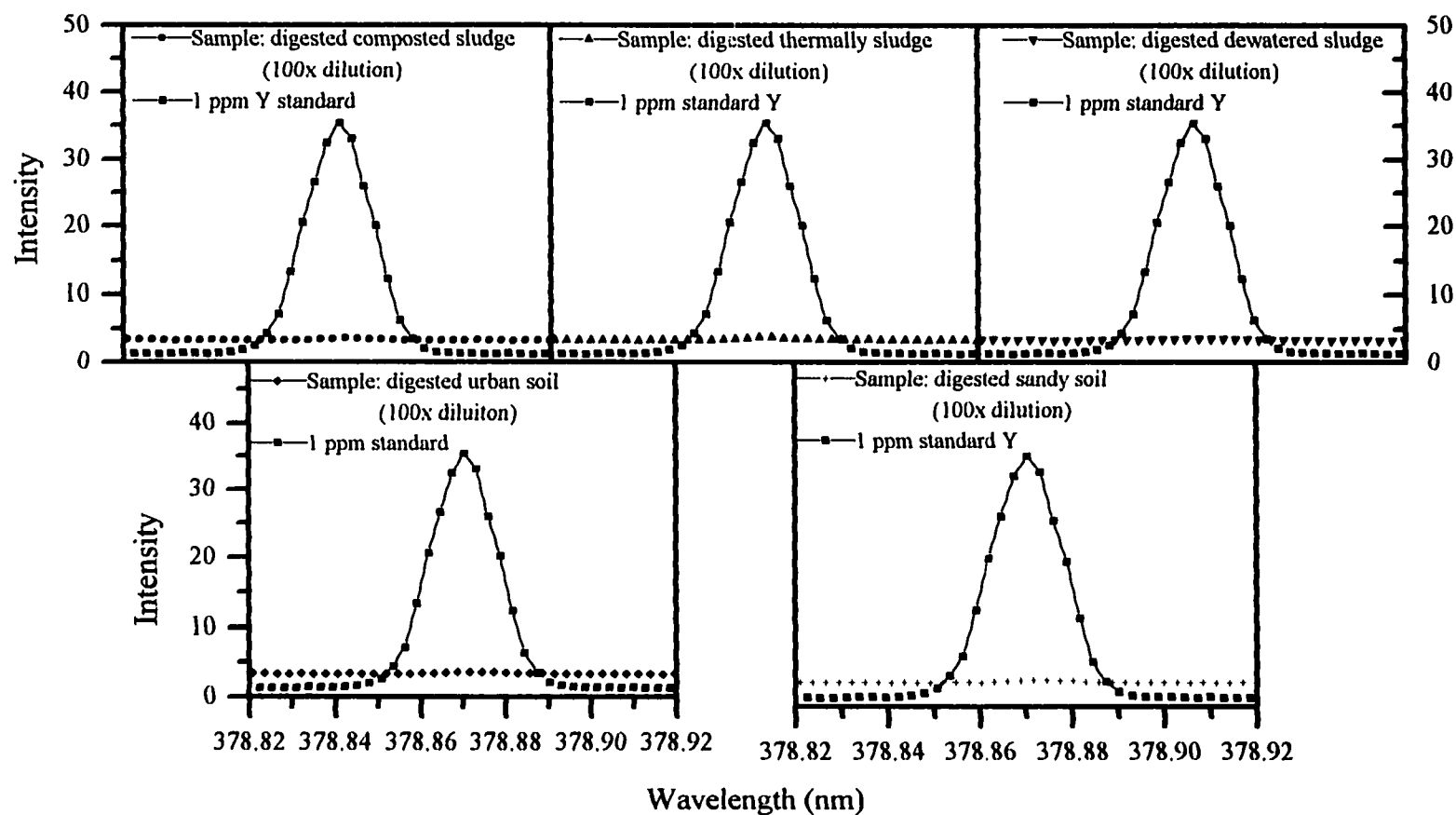


Figure 3.30 Spectra obtained from scanning digested sewages and soils samples surrounding the Y emission line at 378.870nm, the horizontal lines, 10s integration; peaks from spectra of 1ppm Y standard solution, 3s integration time.

To further ensure that the added yttrium does not interfere with any analyte line of interest, a 5ppm yttrium standard solution was scanned for all analyte lines listed in Table 3.3 with their corresponding integration times. The spectra for all 11 analyte lines in Figure 3.31 show that Y has no emission at any of the analyte lines of interest.

Figures 3.32 and 3.33 show the calibration curves of Cu with and without using 1 ppm yttrium as the internal standard. With the internal standard, the calibration curve is much improved. Leachate sample 02T40 was measured in the absence and presence of 1 ppm of yttrium as the internal standard. The relative standard deviations were then calculated from 11 successive measurements. The values of the relative standard deviation obtained from these experiments are listed in Table 3.4. From the results, it can be concluded that the precision is improved by the internal standardization.

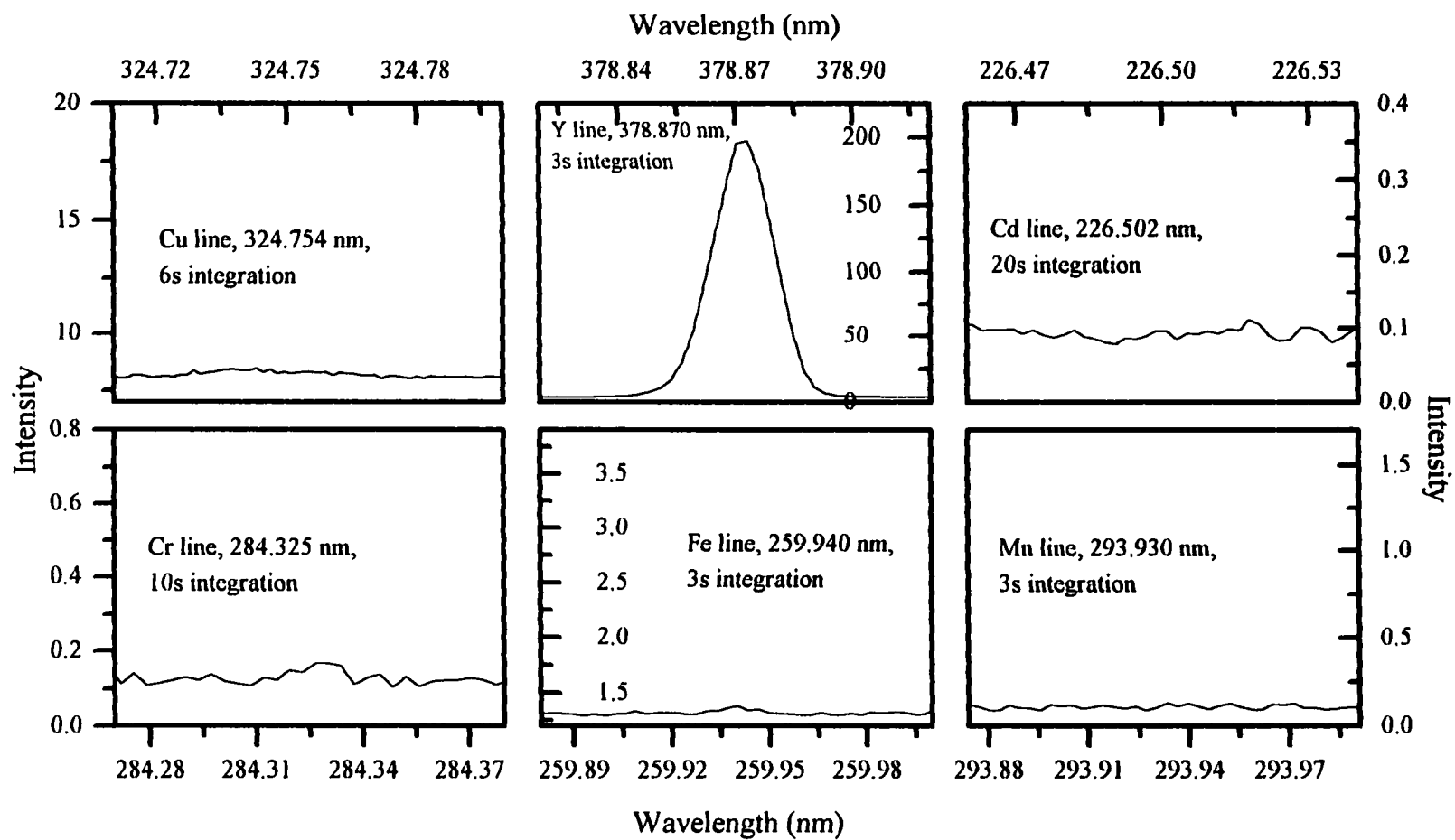


Figure 3.31 Spectra obtained from scanning 5 ppm Y standard solution surrounding 11 analyte wavelines interest.

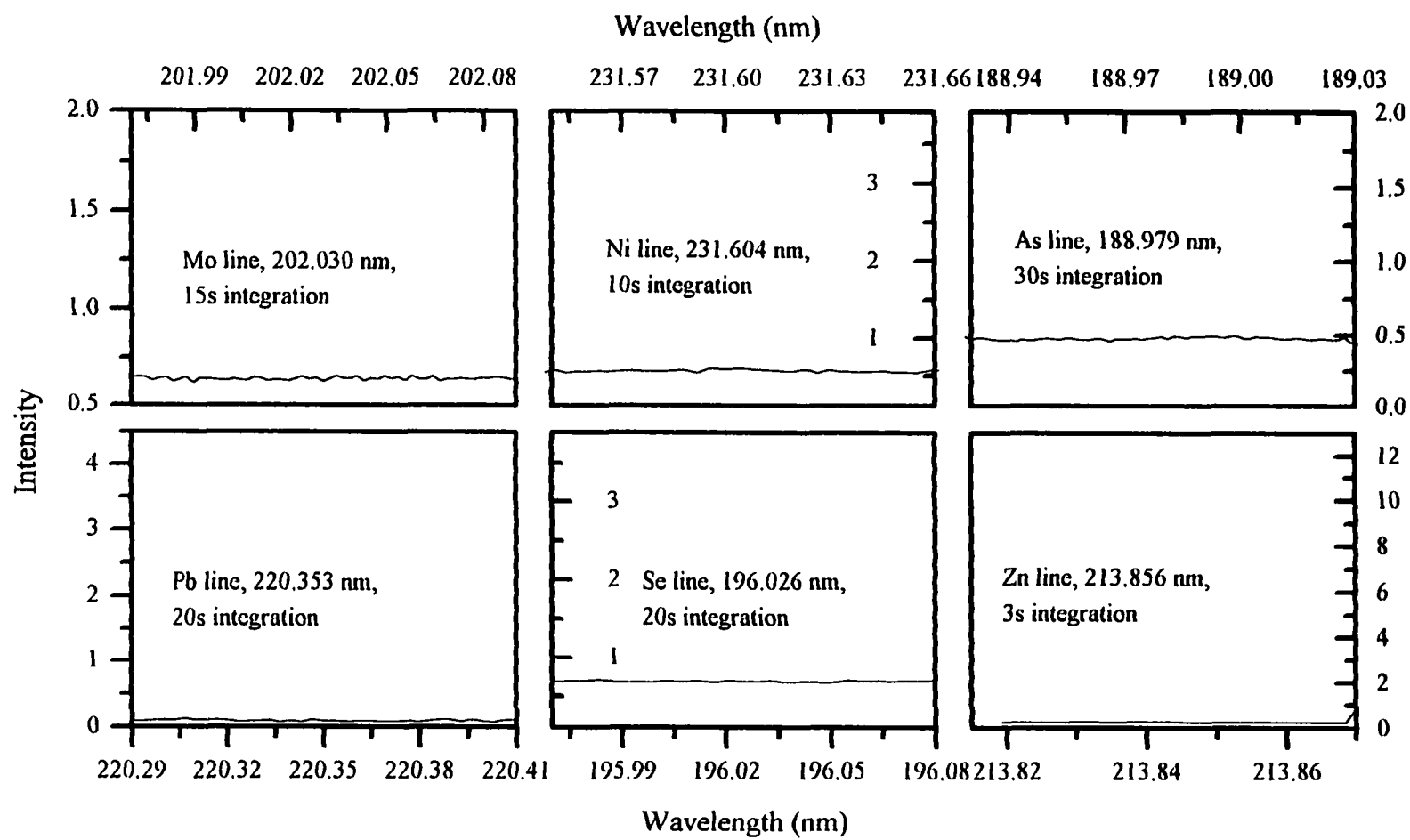


Figure 3.31

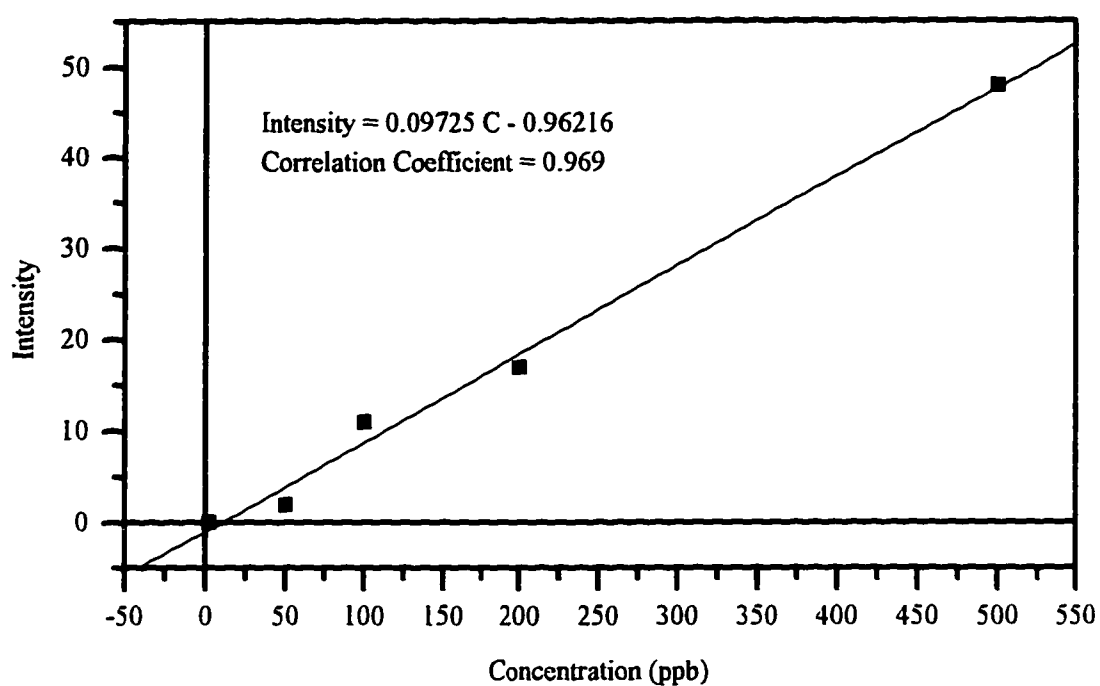


Figure3.32 Calibration Curve for Cu without internal standard.

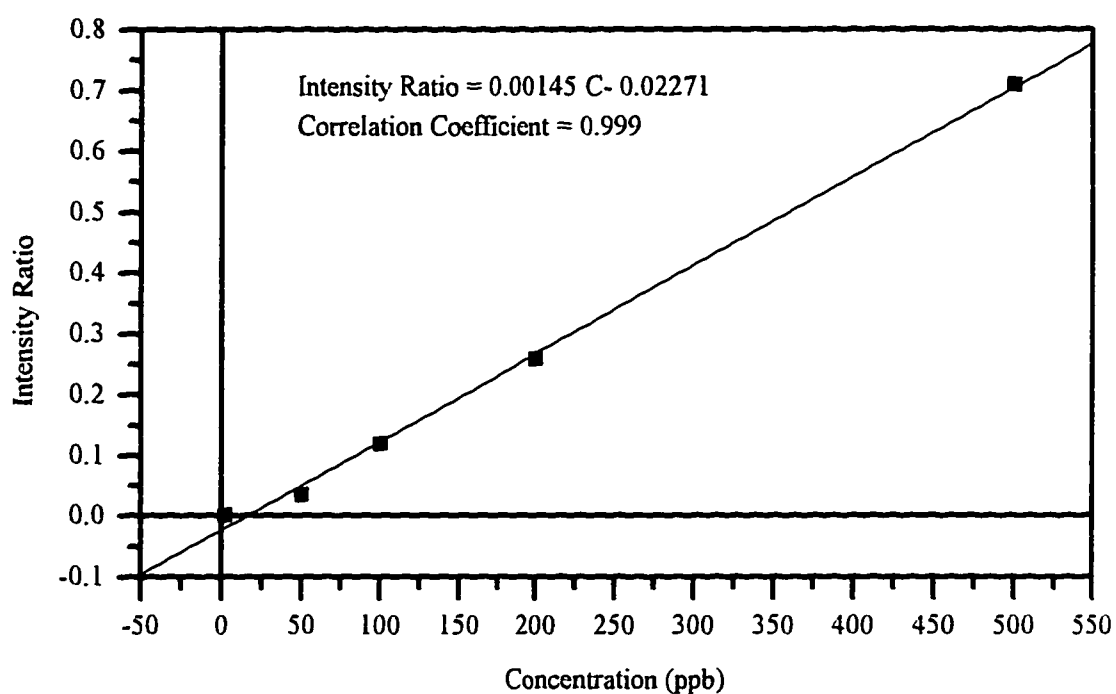


Figure 3.33 Calibration Curve for Cu with 1 ppm Yttrium as internal standard.

Table 3.4 Precision using the USN with and without internal standardization (%RSD, n=11)

	As	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Zn
Without I.S.	2.49	1.45	5.34	3.25	1.34	1.47	7.25	3.76	4.61	5.17	1.18
With I.S.	1.36	0.75	1.89	1.23	0.94	0.85	4.25	1.44	1.15	2.35	0.78

In order to further investigate the resistance of the internal standardization method to instrumental drift, Cu concentrations were determined with different instrumental conditions to compare with that in the standard calibration, in which six standards were calibrated at the conditions listed in Table 3.1 and 3.3. The instrumental conditions were changed manually as follows:

Forward power: 1190, 1195, 1200, 1205, 1210, 1215, 1220.

Peristaltic pump rate; 1.5 mL/min., 2.0 mL/min., 2.5 mL/min.

As seen in Figure 3.34 and 3.35, sample taking rates of the nebulizer and forward power that drift within 1%, do not affect the determination accuracy at all with the internal standardization method. However, the intensity measurement of the Zn line in sample 03TS40 without internal standardization increased with increase in pump rate since more analyte is taken up to the nebulizer (Figure 3.36), although the intensity of Zn line shows only minor increase with the forward power increase within 1% (Figure 3.37).

When matrix matching is not possible, the method of standard addition should always prove helpful in ICP-AES because of the long linear calibration ranges. However, standard additions will considerably increase the analysis time because of the vast number of samples analyzed. Internal standardization was proven to be an ideal alternative to compensate for the effects of physical properties of the liquid, such as density, viscosity, and surface tension, on both the pump rate and nebulization in terms of simplicity. In addition, because the intensity of

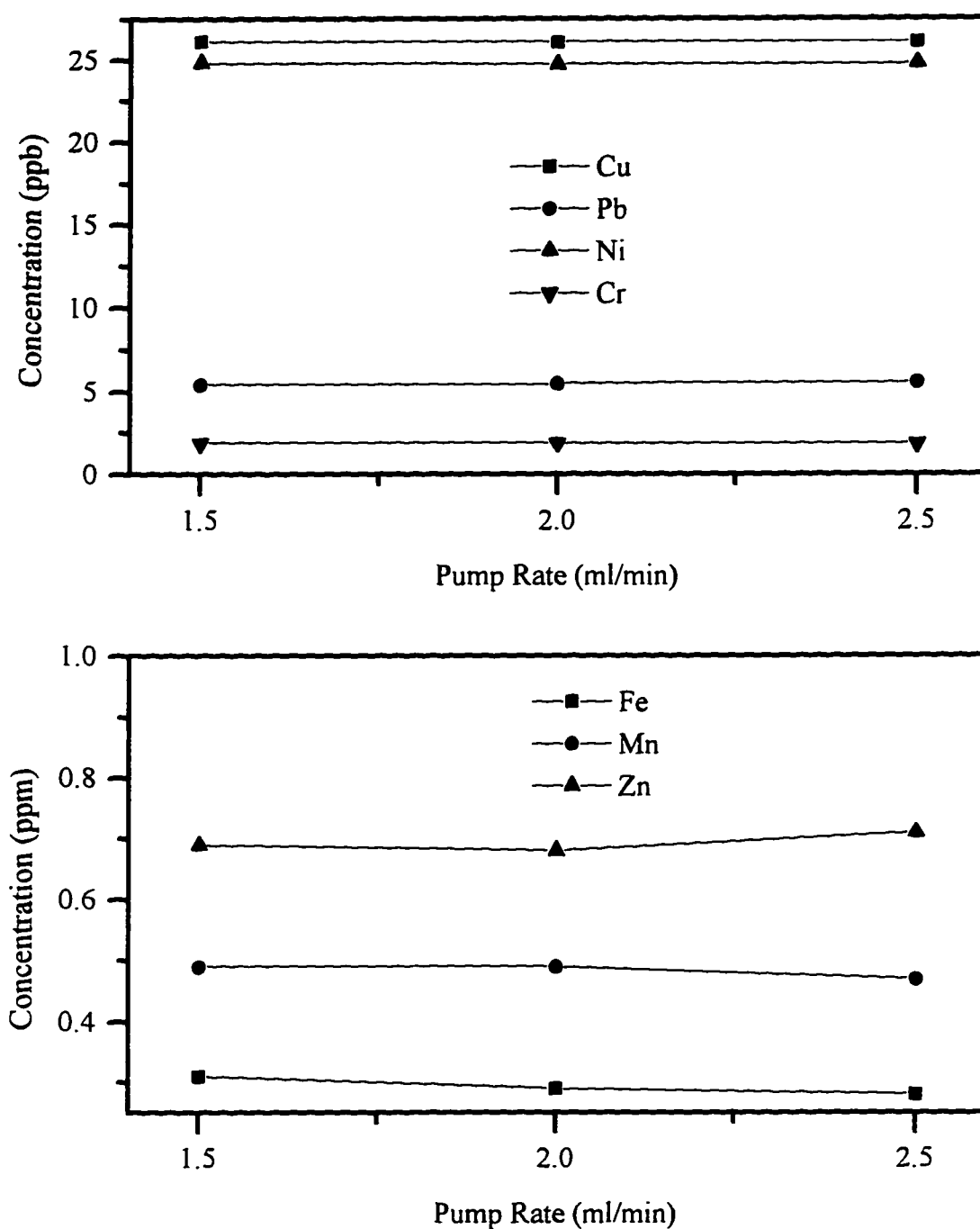


Figure 3.34 Concentration vs peristaltic pump rate with 1ppm Y as internal standard added to all samples and standards. The instrument was calibrated by standards at pump rate 2.0 ml/min and forward power 1200. Sample 02TS40 was taken up using different pump rates.

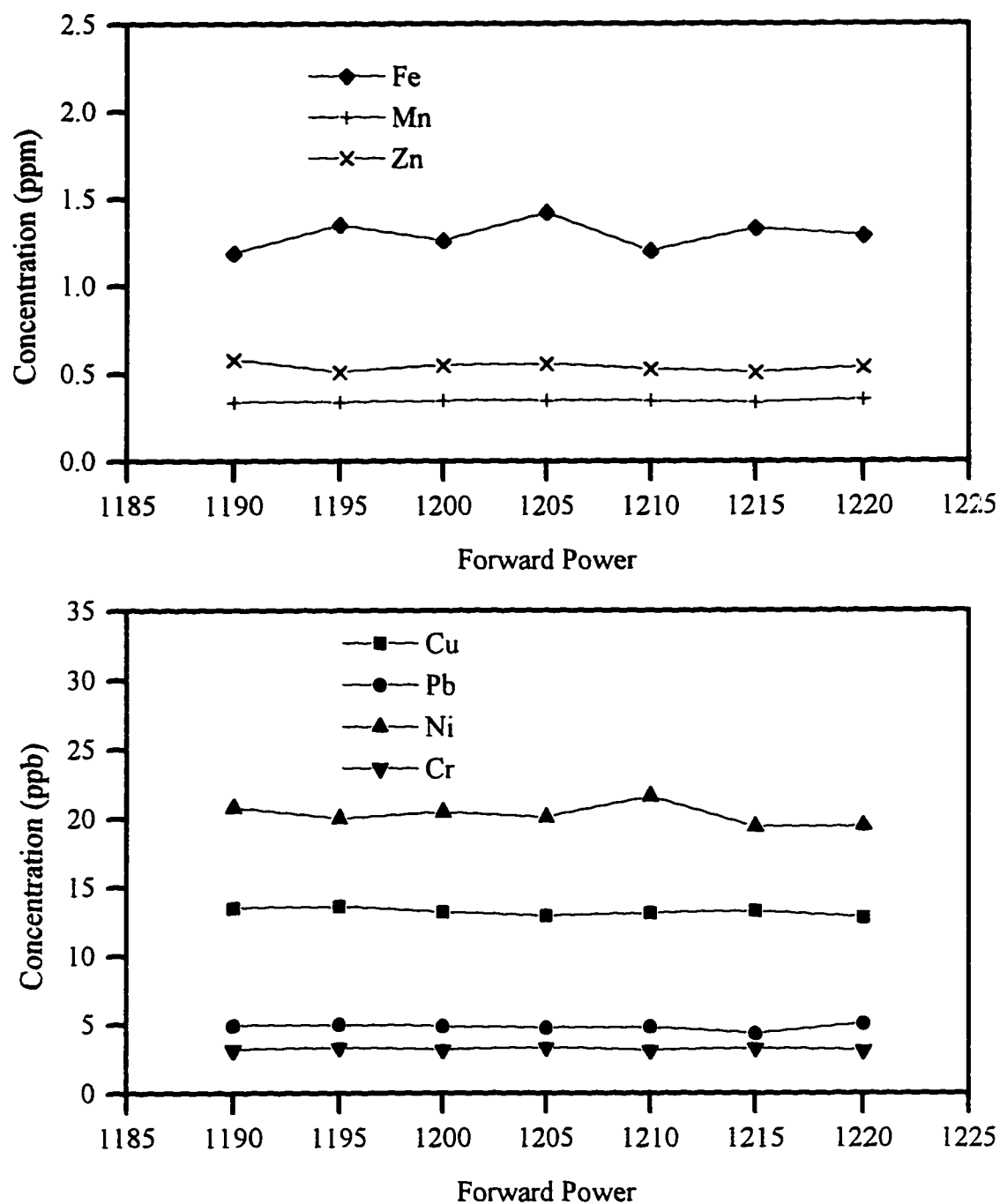


Figure 3.35 Concentration vs forward power with 1ppm Y as internal standard added to all samples and standards. The instrument was calibrated using standards at a pump rate 2.0 ml/min and forward power 1200. Sample 02TS40 was determined using different forward powers.

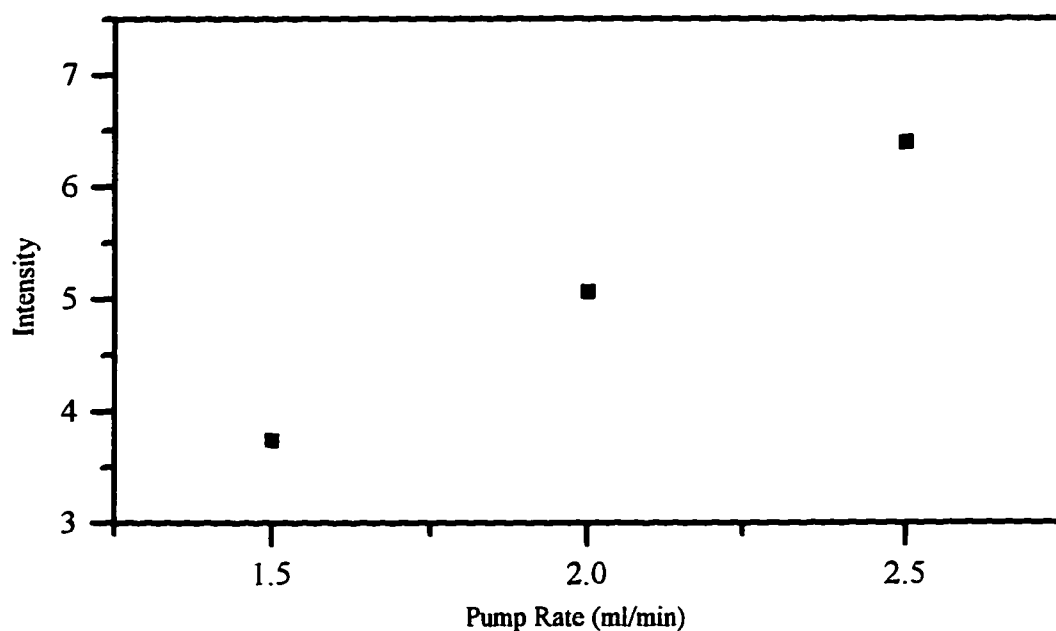


Figure 3.36 Intensity of Zn line at 213.856 nm vs pump rate for sample 02TS40 without using internal standard, forward power 1200.

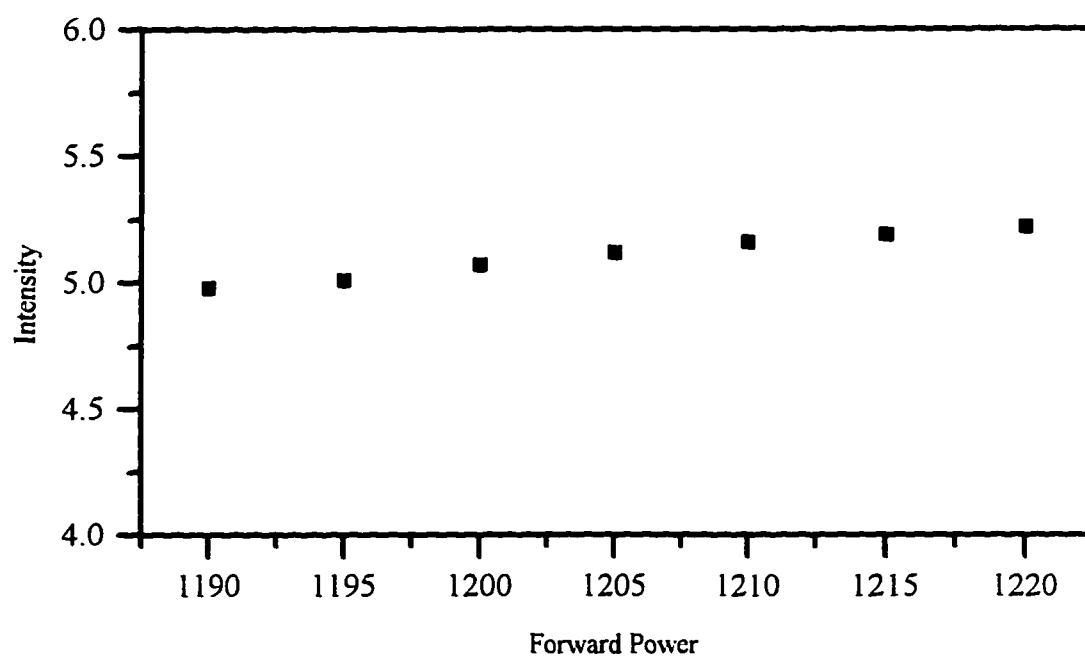


Figure 3.37 Intensity of Zn line at 213.856 nm vs forward power for sample 02TS40 without using internal standard, pump rate 2.0ml/min.

the internal standard Y is determined immediately after each analyte line, the internal standardization provides an efficient way to correct the short term and long term instrumental drifts, obviating the need of running the calibration standards frequently.

3.9 Interelement Interference Correction

Because some elements with secondary emission lines (especially Fe) appear in relatively high concentrations in the leachate solutions relative to the trace elements of interest, even a small overlap in spectral emissions could introduce substantial error in estimation of the trace elements. Thus, it was necessary to calculate interference factors for some of the heavy metals of concern [76]. This was accomplished by constructing calibration curves of the analyte lines of interest with Fe at high standard concentration. Figure 3.38 shows the Fe interference on the calibration curve of Pb at 220.353 nm. First, the Pb standards used in all leaching experiments were calibrated at 20.353 nm, then 6 Fe standards at concentrations of 10 ppm, 50 ppm, 100 ppm, 150 ppm, and 200 ppm were run at the Pb analyte line 220.353 nm to set up a interference calibration curve. The apparent Pb response from Fe interference was determined from the calibration curve after the Fe concentration was determined in leachate samples. The Pb concentrations in leachate solutions were then corrected by subtracting the response contributed from Fe interference.

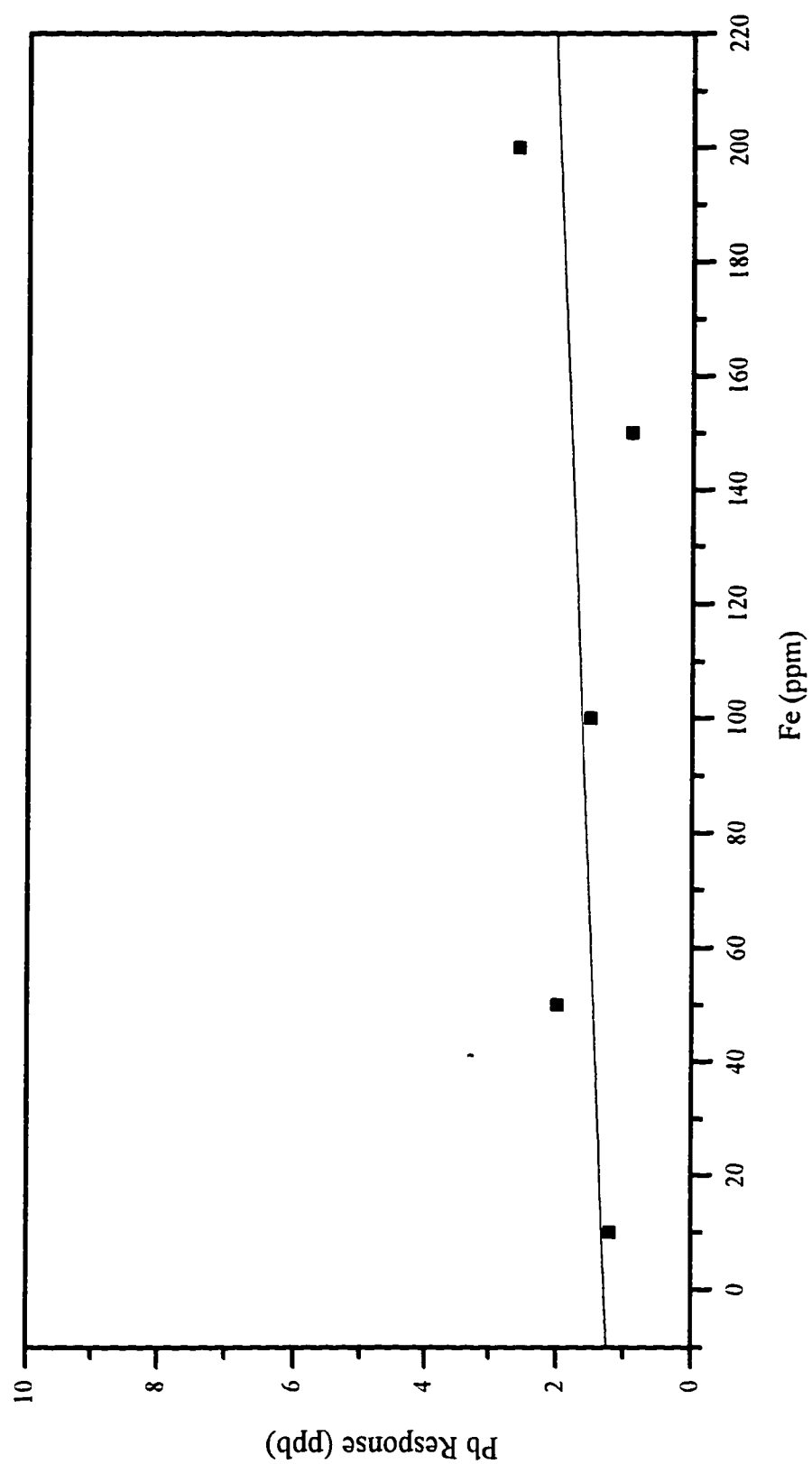


Figure 3.38 Apparent Pb response from Fe interference

Although the literature indicates the high possibility that Fe may interfere in the determination of other elements[77], it was found that the interferences of Fe to all analyte lines studied in this research were not significant, possibly due to the fact that the Fe concentrations in all leaching samples were not so high as that in the literature [77]. Figure 3.38 indicates that Fe does not interfere with Pb determinations over the Fe concentration range of 10 to 200 ppm.

Chapter 4 Leaching Experiment and Results

4.1 Soil Sample Collection and Preparation

The two types of soil used in the sludge-soil leaching experiments were a sandy soil and an urban soil. Sandy soil was sampled from a site in Locust Valley on the North Shore of Long Island (identified as "LIS" in the text). This soil is dominated by Alton stony loam, and is medium to fine brown or reddish yellow sandy loam and gravel. Figure 4.1 is a local map which indicates the sampling site. Samples were taken below the blanket of leaf litter, where the soil has an unusually uniform texture and chemistry.

The urban soil was collected from a garden at the corner of Wyckoff Street and Bond Street, Brooklyn (Figure 4.2), (identified as "BKLYNS" in this context). This soil, initially influenced by alkaline brick and mortar rubble as well as urban dry deposition, has been enriched over 15 years with application of compost. The humus-rich properties of this soil is expected to retain heavy metal by a cation exchange mechanism.

The sandy soil was placed in polyethylene bags and the bulk urban soil was placed in a covered polypropylene barrel. Both types of soil were stored at 4°C in a refrigerated room[78]. Soils were sieved through a 1.6 mm screen to remove large particles before use.

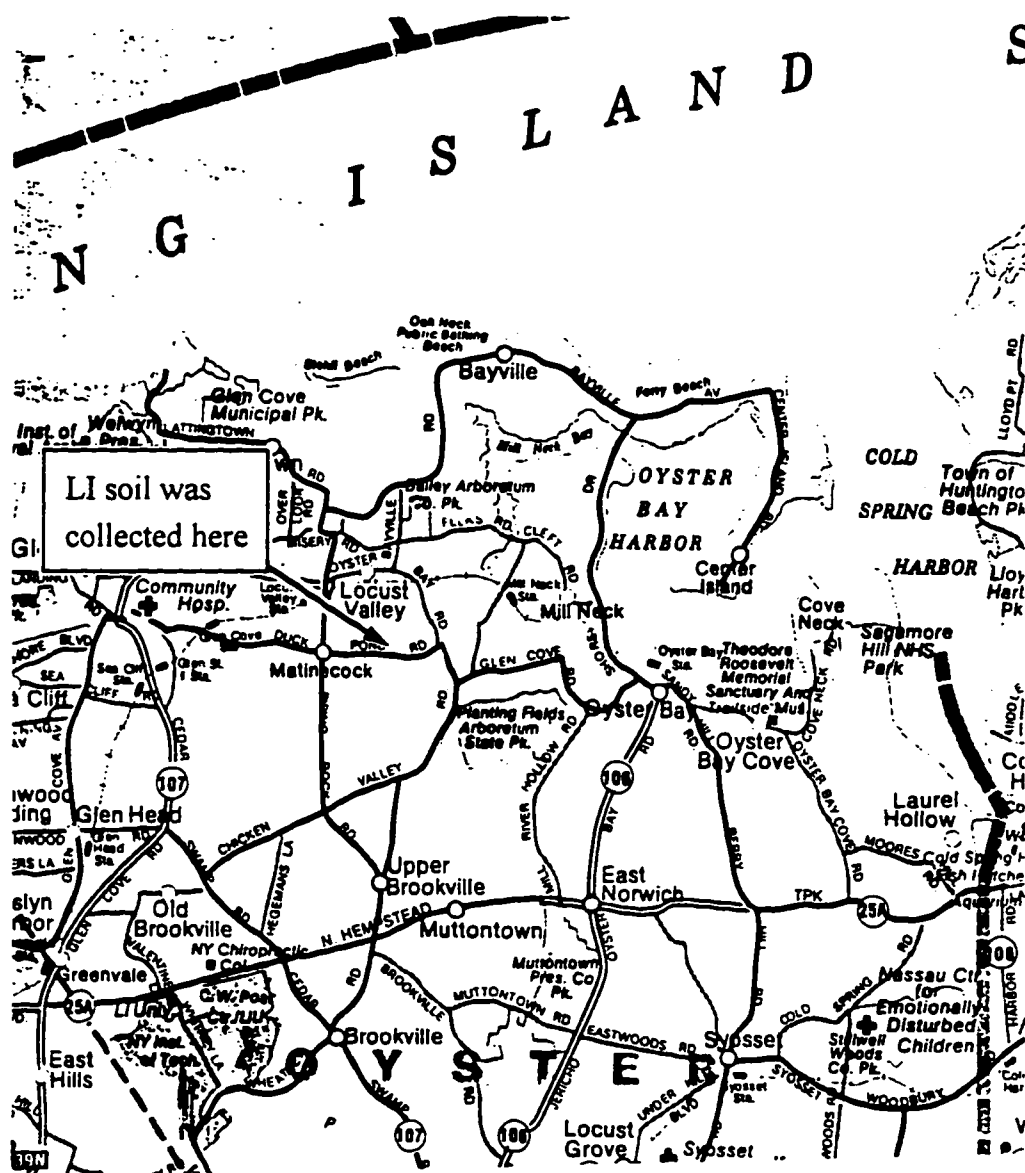


Figure 4.1 Location in Long Island, New York from which LI soil was sampled

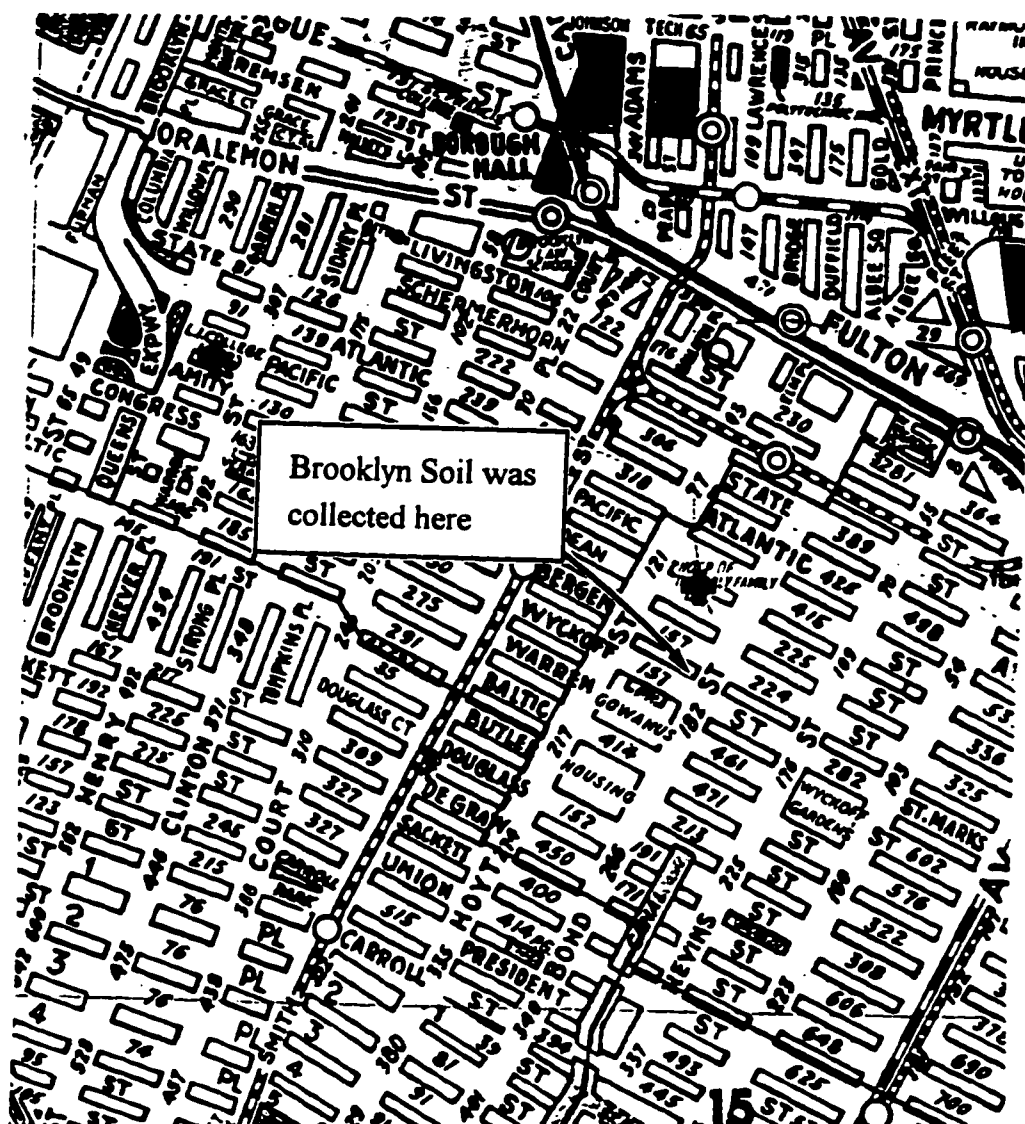


Figure 4.2 Location in Brooklyn, New York from which Brooklyn soil was sampled

4.2 Lime requirement test for soil

A lime requirement (LR) is the amount of limestone (CaCO_3) needed by a plow layer of acid soil to increase its pH to a desired level. After application of lime to soil, not only has the soil the stronger ability to immobilize the heavy metals by hydrolysis, but also CaCO_3 itself can stabilize heavy metals by adsorption [79].

Soil pH control by limestone has been practiced routinely in those areas of the United States where leguminous crops (e.g., clover, alfalfa, peas, beans) are grown [4]. Some states require that soils treated with sludge be maintained at a pH of 6.0 or above to minimize the uptake of toxic metals by crops based on EPA guidance. If soil pH is less than the desired level, the LR test can be used to estimate the amount of agricultural limestone required to adjust the pH.

The LR depends on the target pH desired and the current pH of the soil. Specially designed for LR, the SMP single-buffer method [81] is widely adopted for pH determination of soil. The SMP buffer method to determine the soil pH which will be used for the LR calculation is based empirically on a proportion of the acidity neutralized by CaCO_3 and exhaustive displacement (leaching) of acidity to measure LR. Therefore the amount and proportion of acidity of the soil interest are included in a measurement.

4.2.1 SMP single-buffer preparation:

1. 1 liter of SMP buffer is prepared by dissolving the following chemicals in about 500 mL deionized water while stirring vigorously:
 - a. 1.8 g of p-nitrophenol.
 - b. 3.0 g of potassium chromate.
 - c. 53.1 g of calcium chloride dihydrate.
2. Dissolve 0.2 g calcium acetate in about 200 mL deionized water.
3. Mix solutions 1 and 2, and continue stirring vigorously for about 2h.
4. Add 25 mL of triethanolamine.
5. Dilute to 1 L and continue stirring for 6 to 8 h.
6. Adjust the pH to 7.5 with either 4N NaOH or HCl as required.
7. Filter the buffer through a fiberglass membrane if necessary.

4.2.2 pH determination procedure

Measure 10 mL of dry soil samples into beakers. Add 20 mL of SMP buffer and stir with a glass rod to wet the samples thoroughly. Shake soil-buffer samples for 15 minutes at about 200 cycles per minute. Let samples stand an additional 15 minutes and measure the soil-buffer pH using a pH meter equipped with a glass electrode. A two-point calibration was used for standardization (pH = 4.00 and 7.00). In Table 4.1 are listed pH values for the two types of soil. LR values for desired target pH in this project were calculated by SMP empirical equation [81]:

at target pH = 6.0

$$LR = 1.287(BpH)^2 - 19.38(BpH) - 72.79 \quad (4.1)$$

Where LR is in grams of $CaCO_3$ per liter of soil, and BpH is buffer pH of soil.

Table 4.1 Lime Requirements for Two Types of Soil

Soil Type	BpH by SMP	LR ($CaCO_3$) gram per liter soil
LI Soil	5.88	3.25
Brooklyn Soil	6.60	0.9

When initial buffer pH is higher than target soil pH such as Brooklyn soil, the LR is still necessary for leachate to maintain the target pH leached by rain water. An accurate buffer-pH procedure can estimate a LR within about 0.25 unit of target pH. This tolerance probably approaches the accuracy limitation of the better procedures when used with soils having a wide range of properties [81].

Large batches (1 gallon) of each soil with the lime required respectively were made up and stored in a 4°C refrigerator room for later use.

4.3 Cation Exchange Capacity of Soil

The cation exchange capacity (CEC) of a soil is a measure of the negative charge present on soil constituents and is an indication of the ability of a soil to adsorb cations. The adsorbed cations are, by

definition, exchangeable with the soil solution, and hence are leachable. When sludge is applied to soil, the sludge adds organic matter, etc., as well as heavy metals in addition to those already present in the soil. It is CEC of the soil that plays an important role in immobilizing heavy metal leachable from sludges [79,82].

4.3.1 Principles

The method used to determine the CEC of the 2 types of soil in this research involves two procedures [83], (i) Saturation of cation exchange sites with Na^+ by "equilibration" of the soil with pH 8.2, 60% ethanol solution of 0.4N NaAc-0.1N NaCl, and (ii) Extraction of Na^+ saturated soil with 0.5N $\text{Mg}(\text{NO}_3)_2$. Total Na^+ and Cl^- are subsequently determined in the extracted solution. The soluble Na^+ from the excess saturating solution, carried over from the saturation step to the extraction step, calculated from the Cl^- determination, may be deducted from the total Na^+ . Thus the exchangeable Na^+ is obtained, which is equivalent to the CEC.

4.3.2 Chemicals and Reagents

1). Saturating solution: 0.4N NaAc-0.1N NaCl, 60% ethanol, pH = 8.2 solution. (all chemicals from Aldrich Chemical Company). The Na^+ to Cl^- ratio in this solution was determined to be 5.10.

2). Extracting solution: 0.5N $\text{Mg}(\text{NO}_3)_2$ solution

4.3.3 Procedure

Weigh samples of 4g to 5g of air dried soil, and place in a centrifuge tube.

step 1. Add 33 mL of saturating solution, stopper the tube, and shake for 5 minutes. Unstopper, and centrifuge until the supernatant liquid is clear (~5 minutes). Decant the supernatant liquid. Add fresh saturating solution, insert stirring glass bar stirring for 10 to 30 sec. to disperse the sediment, and continue as above. Make four successive "equilibrations", discarding the supernatant liquid each time.

Step 2. Add 33 mL of extracting solution, shake for 5 minutes, centrifuge until the supernatant liquid is clear, and decant the extracted solution into a 100-mL volumetric flask. Repeat the extraction steps two more times with fresh extraction solution, and make up to volume.

Determine Na^+ and Cl^- in dilutions of this extracted solution. Chloride is determined so that the soluble Na^+ carried over from the saturation step to the extraction step can be deducted from the total Na^+ to obtain exchangeable Na^+ .

4.3.4 Analysis

Na^+ concentration in the saturating solution is determined by ICP-AES after 250-fold dilution. The extracted solution is diluted 10-fold. The Cl^- in saturating and extracted solutions is titrated with 0.0996N AgNO_3 to the endpoint.

$$\text{CEC} = (\text{Na}_t - \text{Na}_{\text{sol}}) = \text{Na}_t - (\text{Cl}_t)(\text{Na/Cl})_{\text{in sat. solution}} \quad (4.2)$$

Where Na_t is the meq sodium in the extracted solution,

Cl_t is meq chloride in the extracted solution, which comes from excess NaCl carried over from saturating step. $(Na/Cl)_{in\ sat.\ solution}$ is the ratio of Na^+ to Cl^- in freshly prepared saturating solution.

The CECs of the two types of soil used are listed in Table 4.2

These results conform with literature values reported as less than 3 meq/kg for sandy soils and between 30 to 500 meq/kg for urban soils [6,79].

Table 4.2 CEC of LI soil and Brooklyn soil

	LI Soil		Brooklyn Soil	
	#1	#2	#1	#2
Soil Weight (g)	5.01	4.95	6.04	5.56
Na ⁺ (ppm) in extracted soln	241.18	229.43	477.26	461.71
Cl ⁻ (meq/L) in extracted soln	1.99	1.91	2.02	1.96
CEC in meq per 100g	0.67	0.47	17.30	19.04
CEC average (meq/100g)	0.57		18.17	

4.4 Sludge Treatment Process

The potential end uses of NYC's sludge vary by the method of treatment, but all involve applying the sludge to land in one form or another [84]. Use of sludge products on land has the potential for adverse impact on both public health and the environment. Potential impacts on public health may be caused by the presence of various substances, particularly heavy metals, that concentrate in the sludge during the sewage treatment process. Since sludge treatment processes can remove most volatiles, destroy most organic matter and micro-organisms, and dramatically change the sludge physical properties, the sludge treatment process plays an important part in immobilizing heavy metals from leaching.

4.4.1 Dewatered sludge (DWS):

Water pollution control plants produce sludge, and most organic materials are removed from sewage during the treatment process. Sludge produced by water pollution control plants is 97% water and 3% solids. By removing some of the water content using dewatering technologies, e.g. centrifuges, the final sludge weight can be increased to more than 30% solids content, resulting in a significant volume reduction. Transportation is made more practical. Further sludge processing, such as composting, and thermal drying, make treatment even more efficient.

4.4.2 Composted sludge (CPS):

Dewatered sludge is mixed with a bulking agent such as wood chips or leaves, in order to facilitate handling, to provide the necessary structure and porosity for aeration, and to lower the moisture content of the biomass to 60% or less. After about 14 days, the composting rate and temperature decline, the pile is taken down, and the compost is cured and dried.

4.4.3 Thermally dried sludge (TDS):

Thermal drying of wastewater sludge is gaining increased acceptance as a means of reducing the volume of sludge and enabling recycling in the form of fuel or biosolids. The dewatered sludge is passed through a triple-pass rotary dryer in a heated air stream to evaporate water. Temperatures up to 450 °C inactivate all pathogens. Pellets approximately 3 mm in diameter are formed by the turning motion of the rotary pin dryer.

4.5 Heavy metals present in sewage sludge products and soils

The quality of sludge products for land application is determined not only by the nutrient contents but also by its toxic contents available for plant uptake and leachable into the groundwater. Heavy metals are the toxic materials of the most concern present in sewage sludge

products. Their availability to plants and groundwater are directly related to their leachability by rainwater when applied to land. The amount of heavy metal is among the factors affecting the leaching characteristics of heavy metals from the sludge. Therefore heavy metals were analyzed in the three sewage sludge products and two types of soil in this research.

4.5.1 Drying and ashing materials:

Approximately 1 gram of air-dried sample was accurately weighed in porcelain crucible. The sample was dried overnight in an oven at 120 °C, and re-weighed. The water content removable at 120 °C was calculated from the difference in weight. The crucible was then placed in a muffle furnace at 800 °C for 4 hours, cooled, and weighed again. This latter loss of weight, i.e. the loss on ignition, is essentially the amount of organic carbon in the sample (plus any loss of mineral-bound water, etc.). The results are given in Table 4.3.

4.5.2 Acid digestion of the samples:

The dry-ashed residues from the above procedure were transferred to a beaker and heated in Ultrex HNO₃ (J.T. Baker) at nearly the boiling point for one hour in a stainless steel hood. Then HClO₄ was added and the beaker was covered. The temperature was raised to 200 °C for 2 to 3 hours till the digest was clear. The cover was removed from beaker and heating continued at 120°C until the fumes of HClO₄

dissipated. The digested residue was washed out 4 to 5 times with distilled, deionized water (Milli-Q System) and the solution was filtrated through a 0.45 μm filter (Millipore). The digested solution was analyzed by ICP-AES (Refer to Chapter 3). Where necessary, samples were diluted so that their concentration fell within the range of calibration standards. In Table 4.3 are listed the results. The abundant Fe contents in the sludge products reflects the addition of ferrous oxides as part of the sludge conditioning process [84].

Table 4.3 Characterization of Sludges and Soils used in this Research¹

	Thermally Dried Sludge	Composted Sludge	Dewatered Sludge	LI Soil	Brooklyn Soil
%Water	4.94%	50.66%	72.3%	0.75%	4.11%
Loss on Ignition	56.15%	15.77%	18.5%	1.89%	8.56%
TOC by Titration	13.3%	15.6%	15.2		4.9%
As	7.3	7.7	7.2	1.5	4.1
Cd	8.5	6.9	8.6	1.6	2.3
Cr	139	132	148	3.5	5.0
Cu	829	1053	1177	2.8	55
Fe	2.28%	2.57%	1.93%	1.41%	1.45%
Mn	591	597	299	144	225
Mo	5.8	7.3	13	2.2	2.2
Ni	59	55	90	22	39
Pb	164	395	206	26	470
Se	0	7.1	0	12	0
Zn	1244	1022	1435	43	91

¹ Elemental concentrations are based on the dried (120°C) samples, in ppm unless noted as % for Fe.

4.6. Leaching experiment design

4.6.1 Column construction:

Fourteen leaching columns were built with the 3 sludges, 2 soils, and the 6 combinations of sludges and soils. 50 mL polypropylene syringes with internal diameter 2.6 cm were used as leaching columns. Fifty grams of air-dried soil or sludge were packed in the syringes (Figure 4.3). The sludge weight used for amending the soils was calculated based on the projected actual rates of application of sludge products to soil [4], i.e. for thermally dried pellets, 8-10 ton/acre/year = 176-220 ton/acre in 22 years; and for composted sludge, 17 ton/acre/year = 400 ton/acre in 22 years. Thus for the thermally-dried pellets, $10 \text{ ton/acre/year} \times 9.072 \times 10^5 \text{ g/ton} \times (2.6 \text{ cm}/2) \times \pi \times 2.471 \times 10^{-8} \text{ acre/cm}^2 = 1.19 \text{ g}$ thermally-dried pellets should be placed on top of 50 g of soil. For the composted sludge, 2.02 g should be mixed with the upper layer of 50 g of soil in the syringes. Table 4.4 lists the columns built with the various packings, leaching conditions and their abbreviations in the context.

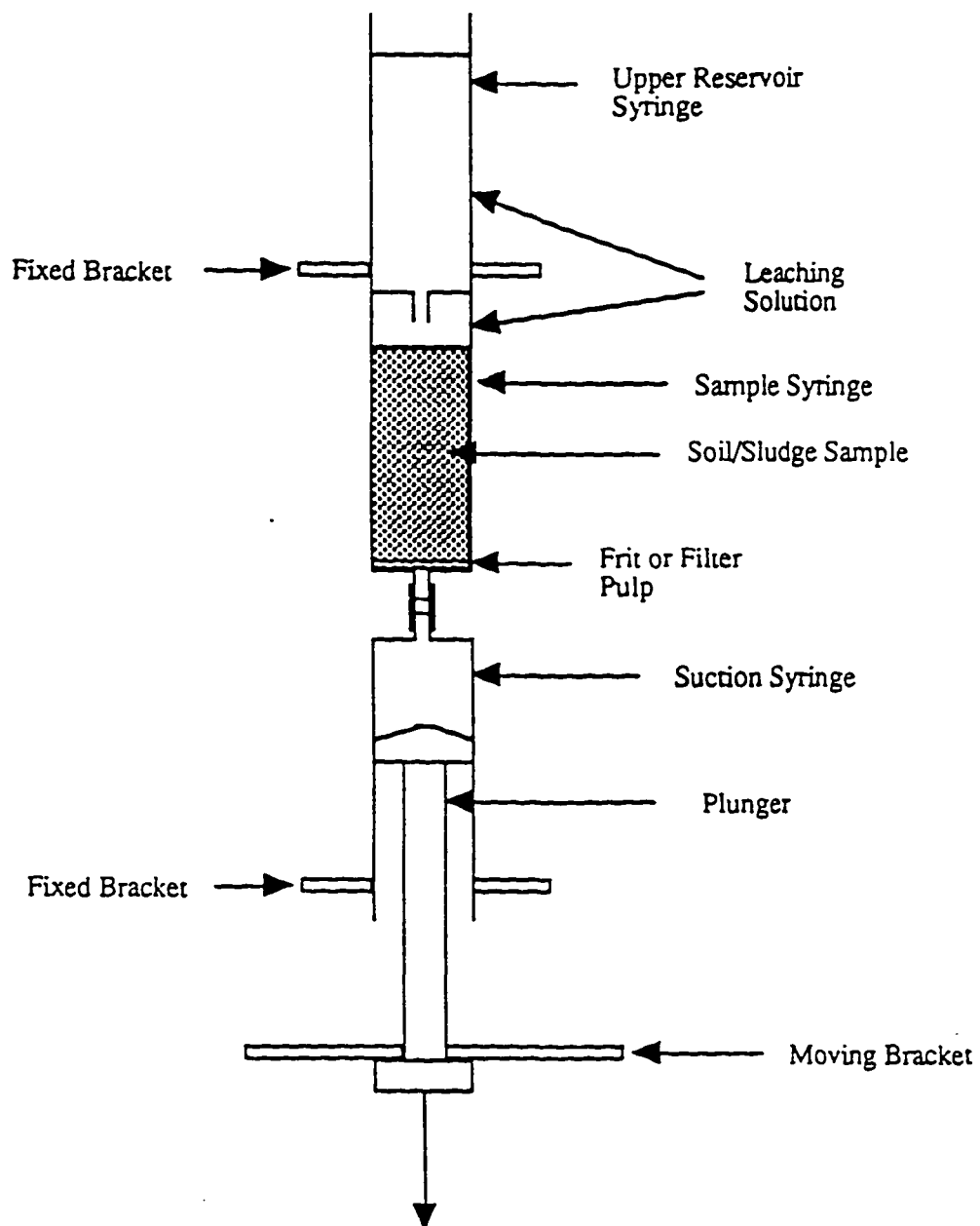


Figure 4.3 Schematic diagram of small-scale leaching apparatus

Table 4.4 Leaching column packings and conditions

Column #	Sewage Sludges (gram)			Soils (gram)		Leaching solution pH	Symbol
	Composted	Dewatered	Thermally -dried	LI	Bklyn		
1				50		1.5	S10
2				50		4.0	S40
3				50		4.5	S45
4				50		7.0	S70
5					50	4.0	R40
6	50					4.0	C40
7		50				4.0	D40
8			50			4.0	T40
9	2.02			50		4.0	CS40
10	2.02			50		4.5	CS45
11	2.02				50	4.0	CR40
12			1.19	50		4.0	TS40
13			1.19	50		4.5	TS45
14			1.19		50	4.0	TR40

4.6.2 Leaching solution

Simulated rainwater of pH 4.0 and 4.5 were the two leaching solutions used initially. These were prepared as need by dilution of a stock solution of pH 1.5 containing sulfuric and nitric acids in a 3/2 mole ratio [85] . All solutions were prepared using glass-distilled water purified using a Millipore Milli-Q System, which provides anion- and cation-exchange deionization, activated charcoal filtration, and filtration through a 0.45 μm filter. The feed water to the glass still was building tap water from the line flushed for 1 hour. Water from the an unflushed line that was then distilled and passed through the Milli-Q system contained several tens of ppb of copper (presumably from the building pipes), which is comparable to the Cu concentrations in the leachates; flushing eliminated this problem. In order to study the pH effect on the leachability of heavy metals, leaching solutions at pH 1.5 and purified water with a characteristic pH 5.6 from dissolved atmospheric CO_2 were also used.

4.6.3 Leaching rate

A mechanical vacuum extractor (Centurion International, Model 24) was used to draw leaching solutions through the soil column at a rate 57 mL/24 h (Figure 4.4). As indicated in the literature [86], this rate of leaching is equivalent to a soil solution residence time of approximately 15 hours and corresponds to the addition of 10.4 cm of precipitation for every day of laboratory leaching. A 15-h residence time was adequate

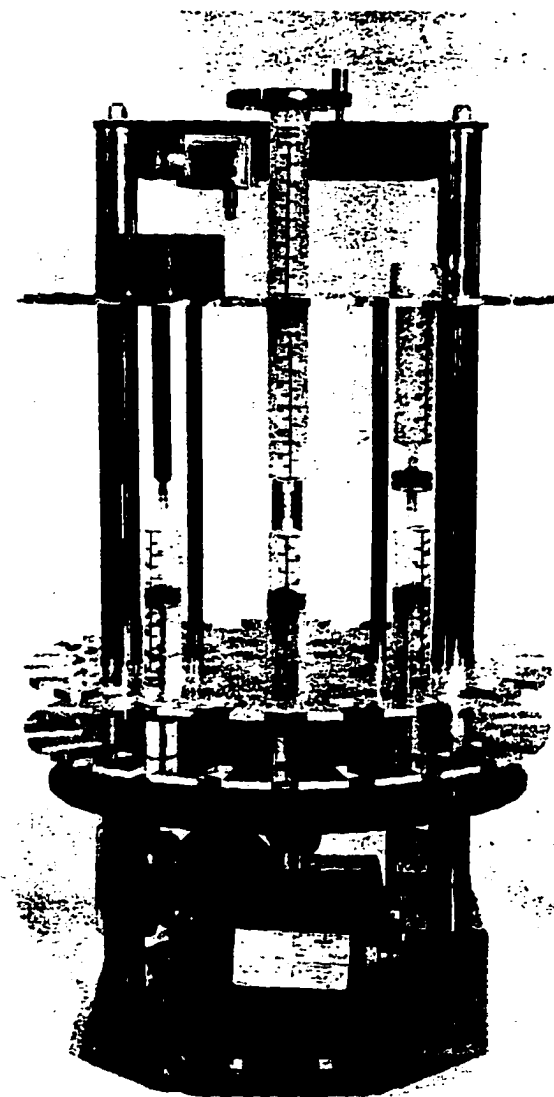


Figure 4.4 Centurion's mechanical vacuum extractor

to allow soil/solution reaction (e.g., exchange reaction, anion adsorption, metal precipitation/dissolution) to reach apparent steady state [80]. Fifty-seven mL effluents were collected daily, and the upper leaching solution reservoirs refilled and leaching continued. Experiments were conducted at a constant room temperature of 25°C. The leachates were filtered through a 0.45 μm filter, and the pH of the leachates was determined immediately upon sample collection. Then concentrated Ultrex HNO_3 was injected into the collected leachate samples to make the concentration of HNO_3 in leachates to be 0.2% w/w in order to preserve the metals.

4.7 Results and Discussion

4.7.1 Buffer capacity of lime-treated soils

To buffer the 50 g of LI sandy soil at pH 6.0, 0.163g (=1.63 mmol) CaCO_3 was used (Section 4.2), which can consume 3.25 mmol of H^+ , i.e. 32.5 L of pH 4.0 leaching solution, neglecting loss of the CaCO_3 by dissolution. At 57 mL/day, 570 days, i.e. 60 times longer than our leaching period (93 days), would be required to neutralize the CaCO_3 . Figure 4.5 confirms the buffer capacity of CaCO_3 treated LI soil leached by pH 4.0 solution. Over the 93 days the effluent pH remained at 6.0. Also, as indicated in Figure 4.6, it would take an even longer time for the pH 5.6 leaching solution to neutralize the buffer capacity of LI soil mixed with CaCO_3 .

The CaCO_3 was physically mixed with the soil, there are three factors in the leaching column that can consume the CaCO_3 and hence reduce the pH buffer capacity of the treated soil.

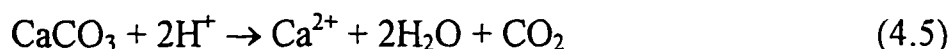
1). The active acidity released from acid groups in organic matter, e.g. carboxylic acid groups, through the reaction



2). The exchangeable Al^{3+} on clays:



3). Reaction with H^+ from leaching solution:



The loss of CaCO_3 in equation (4.5) is not significant when leaching solution pH is 4.0. And the loss of CaCO_3 buffer capacity by

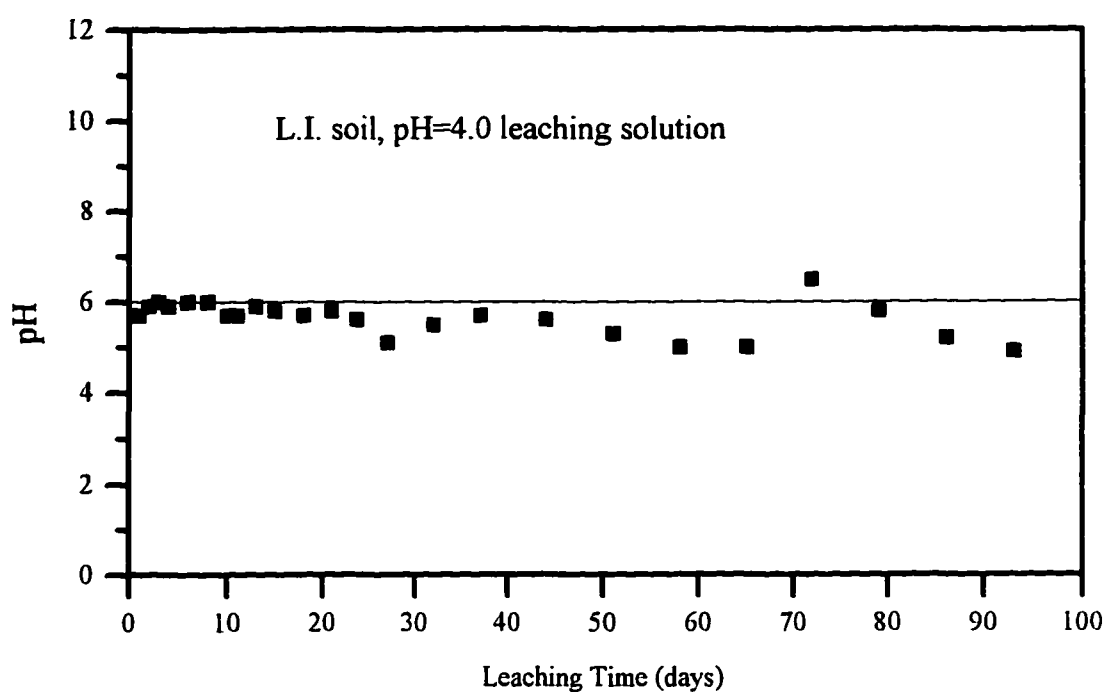


Figure 4.5 pH of leachate vs leaching time. After 93 days leaching with pH 4.0 solution, pH of leachate is still buffered by lime-treated L.I. soil.

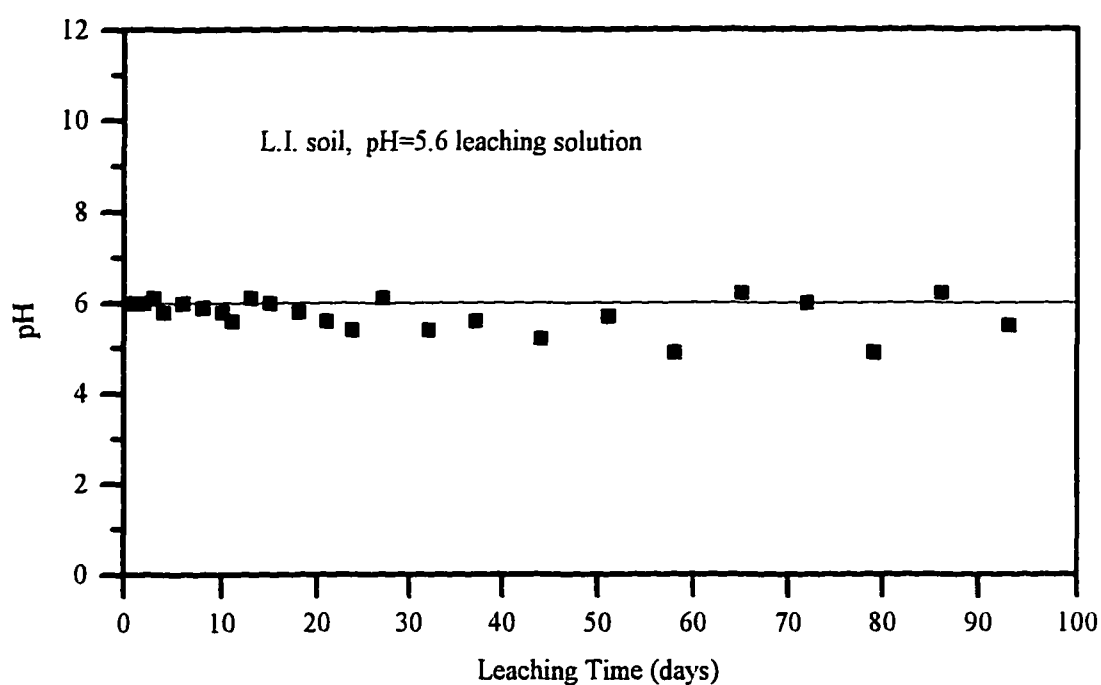


Figure 4.6 pH of leachate vs leaching time. After 93 days leaching with pH 5.6 solution, pH of leachate is still buffered by lime-treated L.I. soil.

all above 3 factors can be also prevented by the reaction in equation 4.4 [87]. The rapidly precipitating $\text{Al}(\text{OH})_3$ coats and protects CaCO_3 particles from further dissolution by soil acidity and leaching solution.

In contrast, only about 100 mL of the pH 1.5 solution would be required to neutralize the CaCO_3 in the column. Obviously, $\text{Al}(\text{OH})_3$ in equation 4.4 can not be formed in this pH value. The depletion of CaCO_3 by leaching solution (equation 4.5) becomes dominant. Figure 4.7 shows the pH of leachates from LI soil drops to pH 1.5 in the first three days.

The pH in leachates from the 3 neat sludge products (only sludge packed in the column) columns leached with pH 4.0 solution all remain at around pH 6.5 (Figure 4.8), although the sludges were not treated with lime before leaching. This indicates that NYC sewage sludges themselves have good buffer capacities against the long-run rain leaching.

4.7.2 Effect of pH on mobility of heavy metals in LI soil

pH of the leaching solution is undoubtedly the dominant factor which determines the solubility of heavy metals. As shown in Figures 4.9a and 4.9b, the availability of potentially toxic elements Pb, Cr, and Ni at pH 1.5 is much greater than at pH of 4.0. The hydrogen ion concentration affects the precipitation of iron and aluminum oxides, and hence the adsorption and desorption of trace elements in and on these precipitates. It also affects the direct precipitation of metallic oxides,

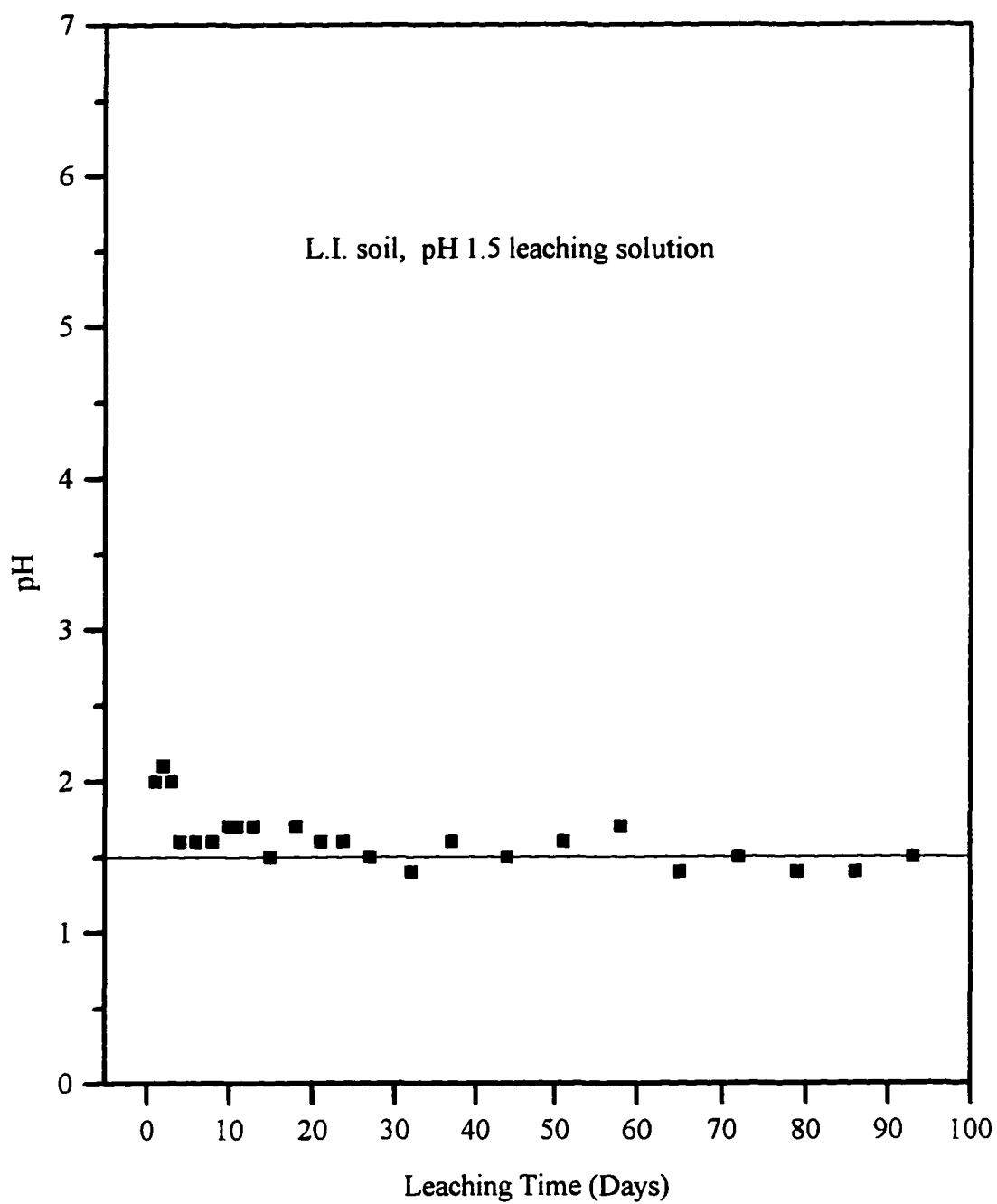


Figure 4.7 pH of leachate vs leaching time. 93 days leaching. After 3 days leaching with pH 1.5 solution, the pH of leachates is around 1.5, the same as the leaching solution.

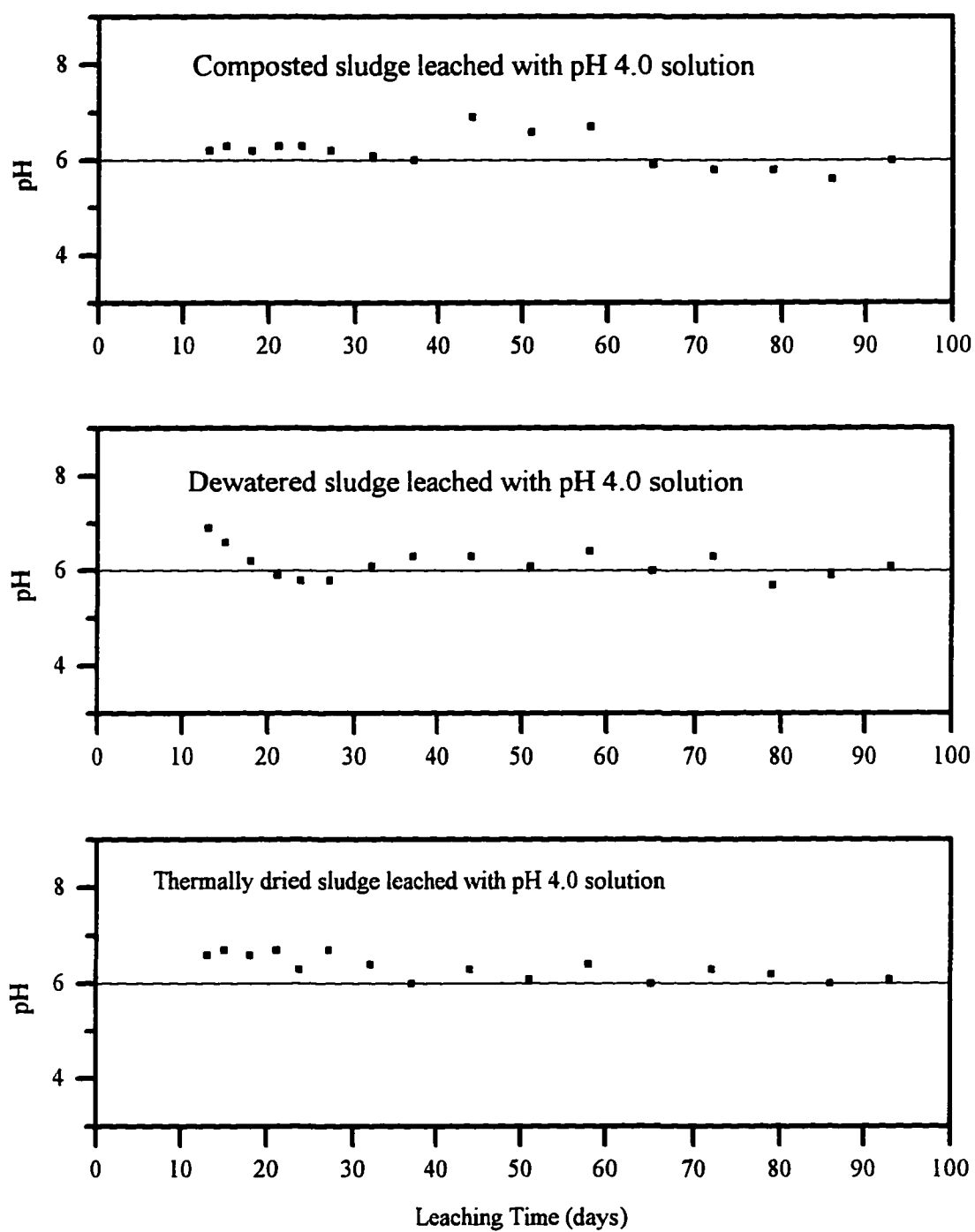


Figure 4.8 pH of leachates from neat sludges leached with pH 4.0 solution vs. leaching time.

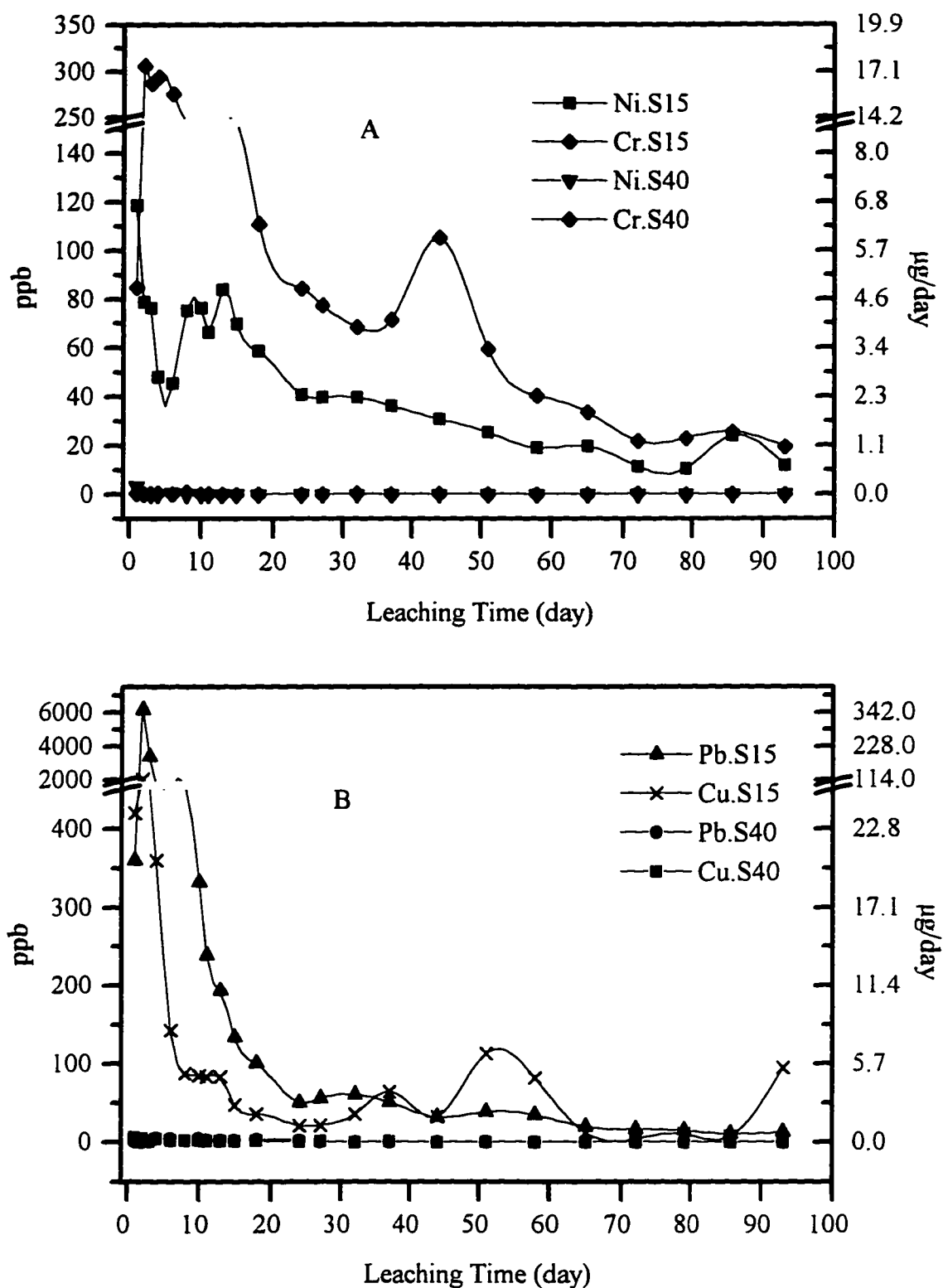


Figure 4.9 Leaching profiles of LI soil at pH 1.5 and 4.0

hydroxides, and carbonates, and the solubility of phosphates. However, contrary to the previous studies by Anderson and Nillson [88], there was no significant difference on leaching of heavy metals by the pH 4.0 and pH 5.6 leaching solutions (Figure 4.10 and 4.11). The reason for these results is clearly related to the buffer capacity of LI soil treated by lime before the leaching experiments discussed previously.

However, the pH effect on the leaching of molybdenum and selenium is reverse to that for all other elements studied. As shown in Figure 4.12, the concentrations of Se in all leachates from pH 1.5 leaching solutions were extremely low or undetectable by ICP-AES at a detection limit of 0.6 ppb. Se and Mo occur in the environment as oxyanions, SeO_3^{2-} , and MoO_4^{2-} . These anions are known to attach to the oxide, to bond to soil organic matter and to mineral surfaces that possess surface hydroxyl groups [89]. The most important minerals in this regard are noncrystalline aluminosilicates; oxides and hydroxides of Fe, Al and Mn; and layer silicate clays. It is the H_2O or valence-unsatisfied OH^- ligands bound to surface metal ions (usually Fe, Al, or Mn) that are the sites of chemisorption. In this case, the surface can be written:



This reaction is favored by low pH, as is evident from the release of OH^- into solution. Low pH causes surface OH^- groups to accept protons, and since H_2O is an easier ligand to displace from metal bonding sites than OH^- , this facilitates the ligand exchange. Therefore, from the point of view of kinetics as well as equilibrium thermodynamics, low pH promotes anion adsorption.

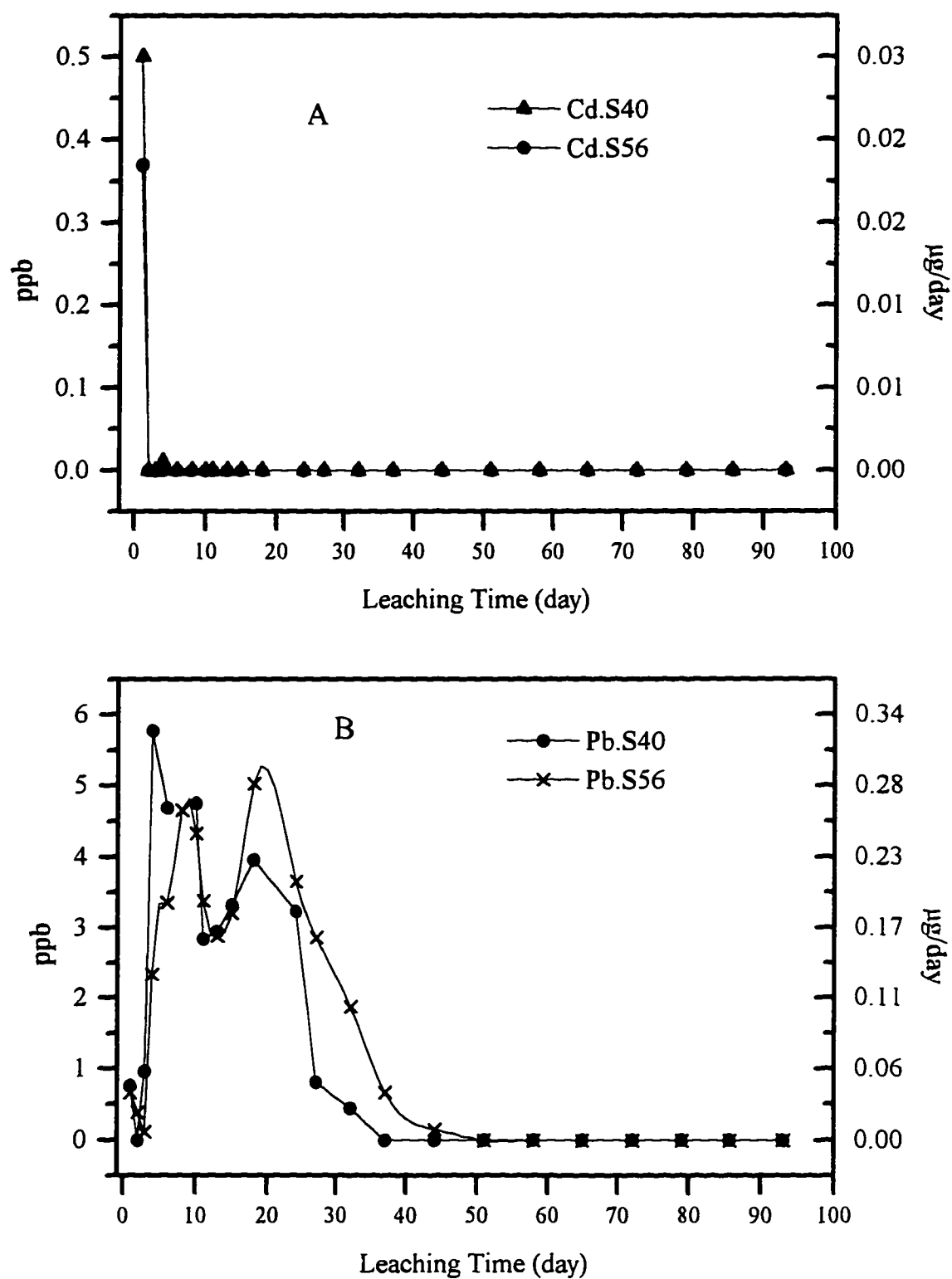


Figure 4.10 Leaching profiles of Cd and Pb from LI soil at pH 4.0 and 5.6

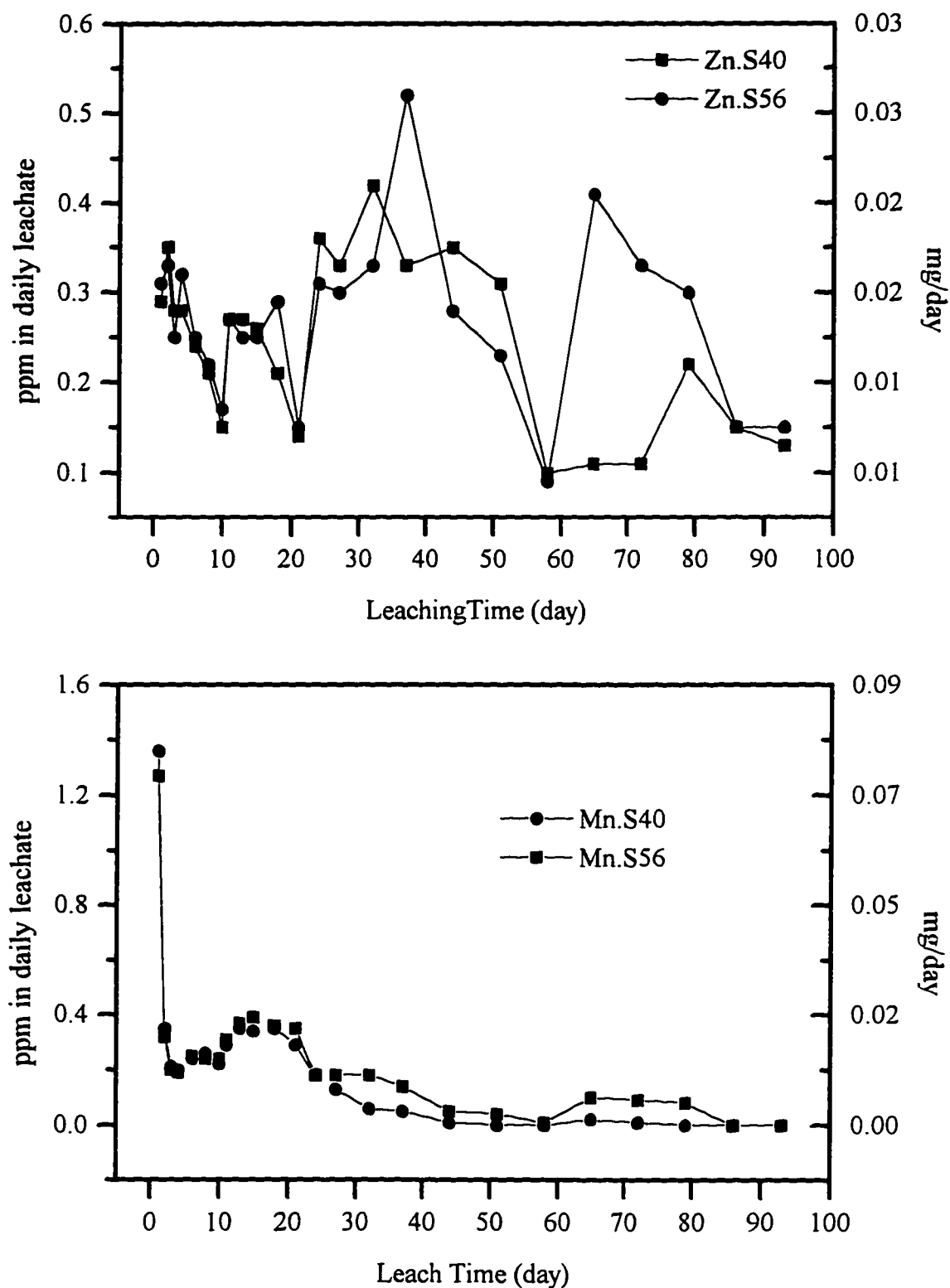


Figure 4.11 Leaching profiles of Mn and Zn from LI soil at pH 4.0 and 5.6

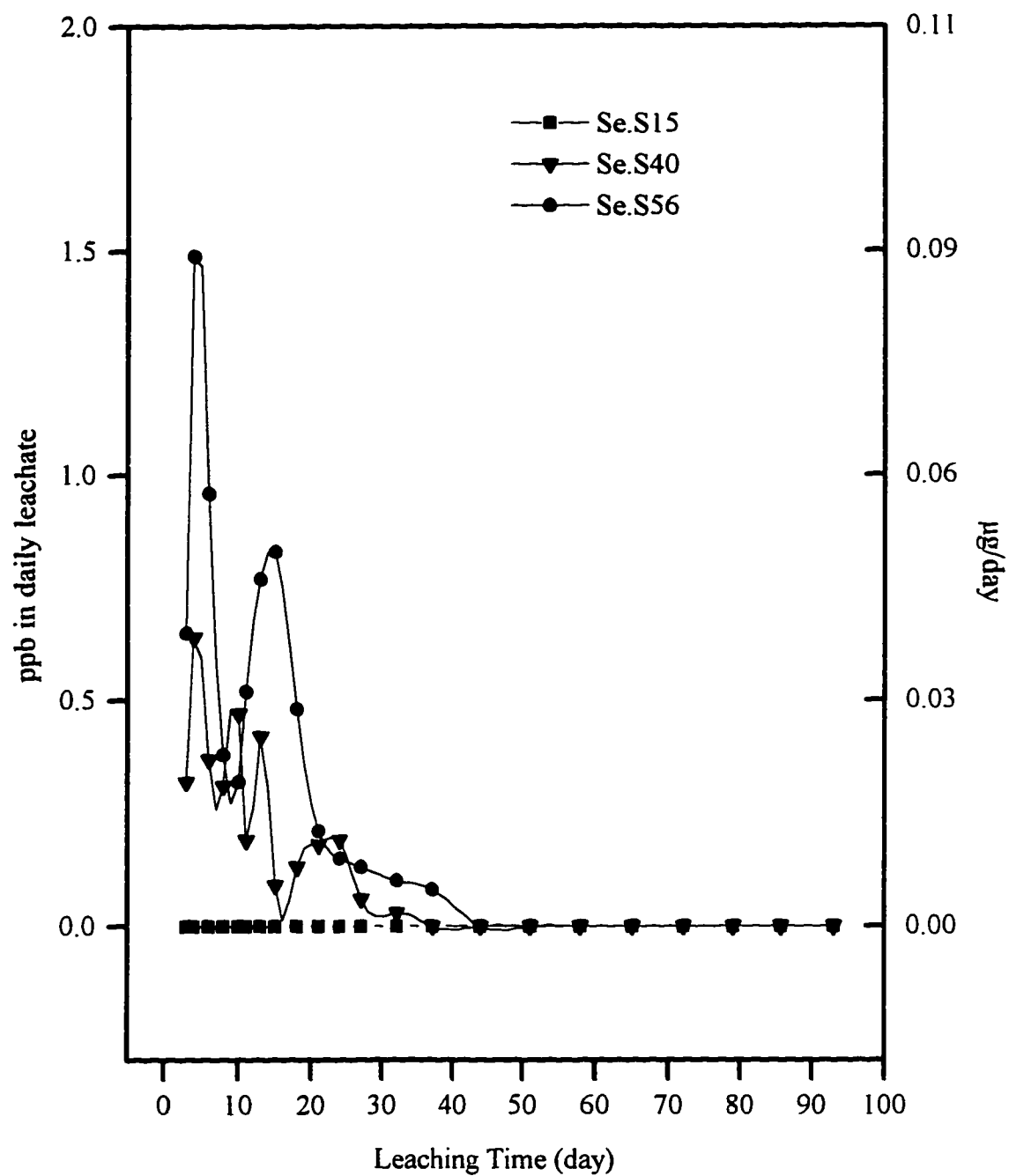
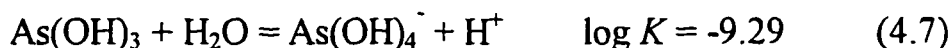


Figure 4.12 Leaching profiles of Se from LI soil at pH 1.5, 4.0, 5.6

It is also found that the leaching of As is not significantly high under strong acidic conditions (pH 1.5) compared to that at pH 4.0 and 5.6, as shown in Figure 4.13. The oxyanions of As play the same role in retention in soil as for Se and Mo. The most probable oxidation states of As in soil environments are +3 and +5 [90]. Arsenate (+5), AsO_4^{3-} , is chemisorbed by Al oxides, noncrystalline aluminosilicates, and its mobility is fairly low in acid soil. However, arsenite (+3), which exists precipitately as As(OH)_3 , behaves like boric acid, forming the anion only at high pH:



The weak acidity of As(OH)_3 causes adsorption of arsenite on oxides and soils to be much weaker than that of arsenate. Therefore, the leaching of As was restrained by lower pH, but not as strongly as Se or Mo elements.

4.7.3 Total amount of heavy metals in sewage sludge products for land application and allowable loading rate of sludge products

Land application of sewage sludge has been practiced in many countries for centuries so that the nutrients and organic matter in sewage sludge can be beneficially used to grow crops or other vegetation. Over the years, land application has been increasingly managed to protect human health and the environment from various potentially harmful constituents typically found in sewage sludge, such as heavy metals. In 1993, the US Environmental Protection Agency promulgated 40 CFR

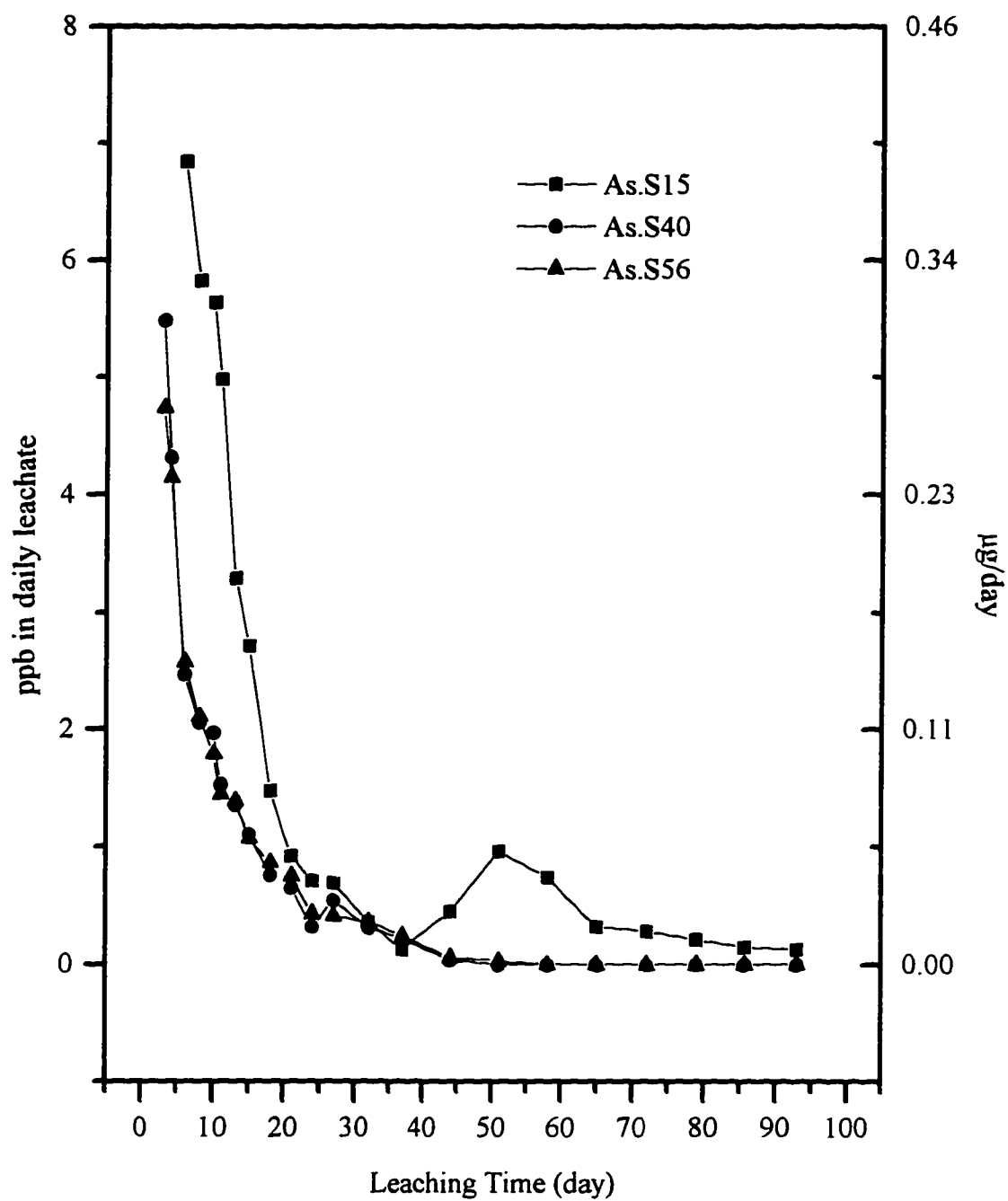


Figure 4.13 Leaching profiles of As from LI soil at pH 1.5, 4.0, 5.6

Part 503 to address the Clean Water Act's requirement that EPA develop a regulation for the use or disposal of sewage sludge.

All sewage sludge applied to land must meet Part 503 ceiling concentration limits (CCL) for the 10 regulated pollutants (Table 4.5). Ceiling concentration limits are the maximum allowable concentrations of pollutant in sewage sludge to be land applied. If the CCL for any one of the regulated pollutants is exceeded, the sewage sludge can not be land applied. The ceiling concentration limits were developed to prevent the land application of sewage sludge containing high concentrations of pollutants. A cumulative pollutant loading rate (CPLR) is the maximum amount of a pollutant that can be applied to a site by all bulk sewage applications. When the maximum CPLR is reached at the application site for any one of the 10 metals regulated by the Part 503 rule, no additional sewage sludge subject to the CPLR is reached at a site; only sewage sludge that meets the pollutant concentration limits could be applied to that site. Table 4.5 lists the 10 heavy metal contents from two sewage sludge products, compost and thermally-dried, which are intended to land application by NYC. It can be concluded from comparing the Part 503 CCL with the each heavy metal concentration in the two sludge products that the quality of these two sewage products, can easily meet the EPA regulation for land application.

Also in Table 4.5 are listed the Part 503 land application pollutant limits. Based on the heavy metal concentrations in the sludge products and annual pollutant loading rates (APLR) for each metal, the annual

whole sludge application rate (AWSAR) can be calculated as follows [4]:

$$\text{AWSAR} = \text{APLR}/0.001 \text{ C} \quad (4.8)$$

where:

AWSAR in the unit of dry metric tons of sewage sludge/hectare/year,

APLR = annual pollutant loading rate (kg of pollutant/ha/yr),

C = heavy metal concentration in ppm on dry basis.

The annual whole sludge application rate (AWSAR) for the sewage sludge products is the lowest AWSAR calculated for all 10 heavy metals. For thermally dried sludge, the lowest AWSAR is for copper at 90 metric tons of sludge/hectare/year. Therefore, the AWSAR to be used for this product is 90 metric tons per hectare/year. This is equivalent to 1845 pounds per 1000 square feet. However, for composted sludge, lead concentration is the determining factor for AWSAR, i.e. only 38 metric tons of compost sludge/hectare/year can be used for land application.

Obviously, the method of sewage sludge processing determines the usage of sludge products for land application. Thermal drying is one of preferred processes in long range sewage sludge management plan of NYC. This process especially affects the mercury content of the sludge product [91]. Hg is the most volatile; it has a vapor pressure of 0.16 Pa at 20°C, which accounts for a saturation concentration of 14 mmHg/m³ air. When exposed to reducing conditions or when heated above 500°C, the mercury compounds are readily decomposed to metallic Hg. It was

reported that more than 97% of the Hg in the sludge was evaporated in a pyrolysis experiment at 350°C [14].

Table 4.5 Heavy metal limits for land application of sewage sludge product

Metal	CCL ppm	APLR	Thermally dried		Composted	
			Conc. ppm	AWSAR	Conc. ppm	AWSAR
As	75	2.0	7.3	274	7.7	260
Cd	85	1.9	8.5	224	6.9	275
Cr	3000	150	139	1079	132	1136
Cu	4300	75	829	90	1053	71
Hg	57	0.85	0.9*	944	7.5*	113
Mo	75	-	5.8	-	7.3	-
Ni	420	21	59	356	55	382
Pb	840	15	164	91	395	38
Se	100	5.0	0	-	7.1	704
Zn	7500	149	1244	120	1022	146

* Results are from Reference 84

APLR in kg of pollutant / ha /yr.

AWSAR in tons sewage sludge / hectare /yr.

4.7.4 Calculation of percentage of heavy metal leached

The total amount of each heavy metal leached from the column was calculated by integration of the daily leaching profile as shown in Figure 4.14 for Cu in LI soil. The percentage (relative to the total metal amount in sludge given in Table 4.3) of heavy metals leached over 85 day period are listed in Table 4.6. The data show that the percentage of metals present in leachates from 3 sludges and 2 soils were less than 7% using pH 4.0 and 5.6 leaching solutions. However, the pH 1.5 leaching solution "washed" out 68% Cr, 73% Cu, 66% Pb, 54% Fe, and 58% Zn present in the LI soil. Similar percentage of As was leached from LI soil with pH 1.5, pH 4.0 and 5.6 solutions, but less Se was leached with pH 1.5 solution than pH 4.0 and 5.6 solution, as discussed in Section 4.7.2 on Figures 4.12 and 4.13.

Among all the metals studied, Zn appears to be the most mobile and Se the least mobile.

4.7.5 Net sludge product leaching

Compare the percentages of heavy metals leached from 3 neat sludge columns by the pH 4.0 leaching solution (C40, D40, T40) in Table 4.6 and Figures 4.15, 4.16, and 4.17, it is concluded that the metals in thermally-dried sludge product show the least mobility. Heavy metals in the composted sludge product show the higher mobility, similar to the dewatered sludge over the 93 day leaching period. Treatment of the sludge changes the chemical form of the metals; most

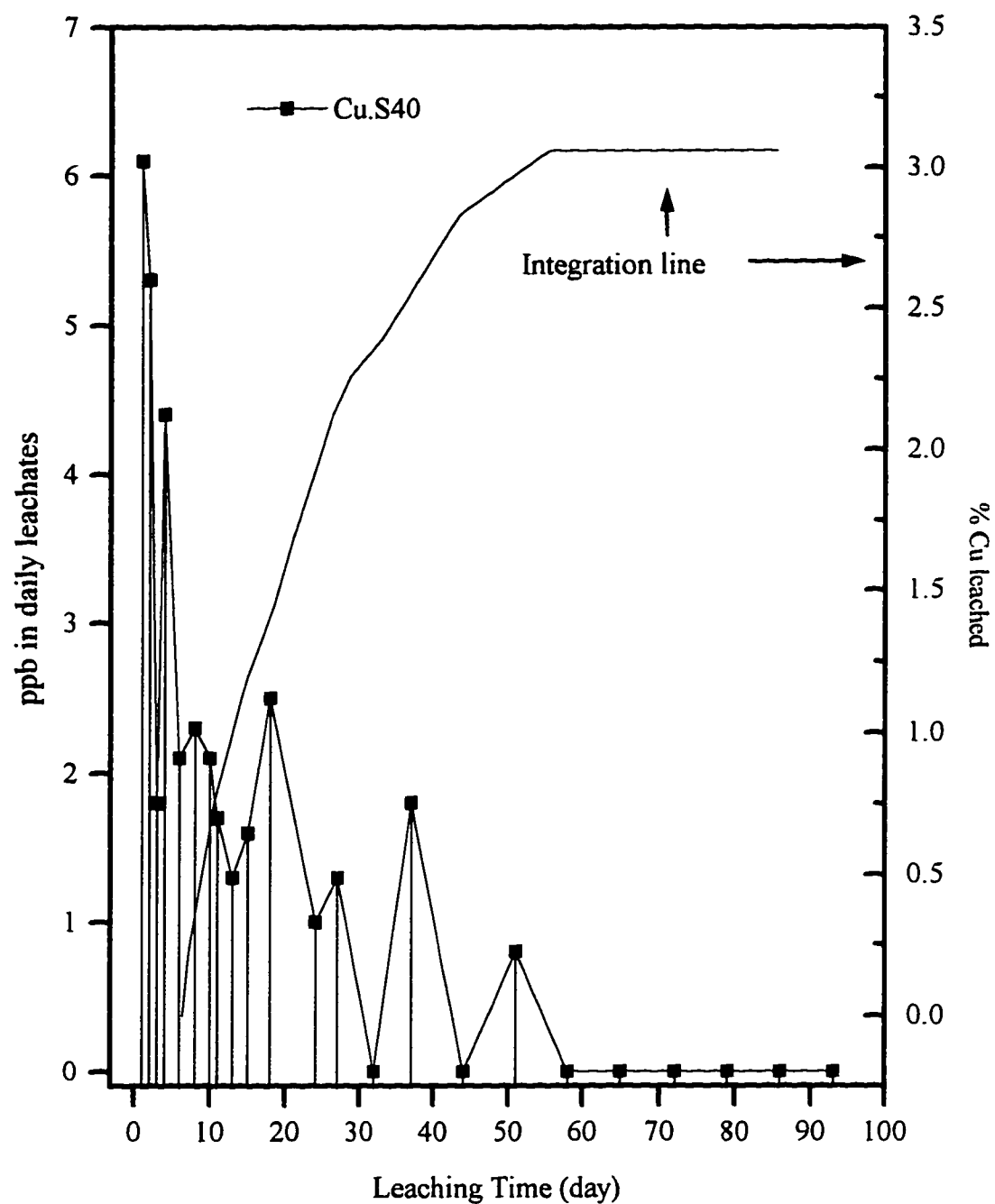


Figure 4.14 Integrations of Cu leached from LI soil by pH 4.0 leaching solution.

**Table 4.6 Percentage of Heavy Metals Leached from leaching Columns
After 85 days leaching**

	As	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Zn
S15	1.16	18.20	68.30	73.10	54.56	45.06	0.16	16.28	65.96	0.14	58.06
S40	0.82	0.02	0.60	3.06	0.15	6.98	0.23	0.09	0.36	0.37	5.63
S56	0.83	0.01	0.38	3.55	0.17	7.11	0.26	0.11	0.49	0.33	6.81
R40	0.78	0.40	2.21	1.64	1.60	1.03	1.02	0.45	0.90		4.16
C40	0.64	0.91	0.82	1.37	2.36	4.12	1.16	1.25	1.41	0.83	3.96
D40	0.33	0.44	0.68	1.11	3.10	3.74	1.70	1.18	1.44		3.21
T40	0.85	0.08	0.25	0.24	1.78	1.52	2.93	0.98	0.04		3.29
CS40	0.71	0.08	1.39	1.00	1.55	2.80	0.45	0.07	1.51	0.10	4.57
CR40	0.80	0.61	2.49	1.70	1.77	1.17	2.98	0.53	0.89	0.93	2.74
TS40	0.85	0.02	0.81	0.55	1.12	2.93	0.00	0.79	1.23	0.19	3.55
TR40	0.77	0.91	1.79	2.05	1.57	1.31	3.77	0.90	0.78		3.49

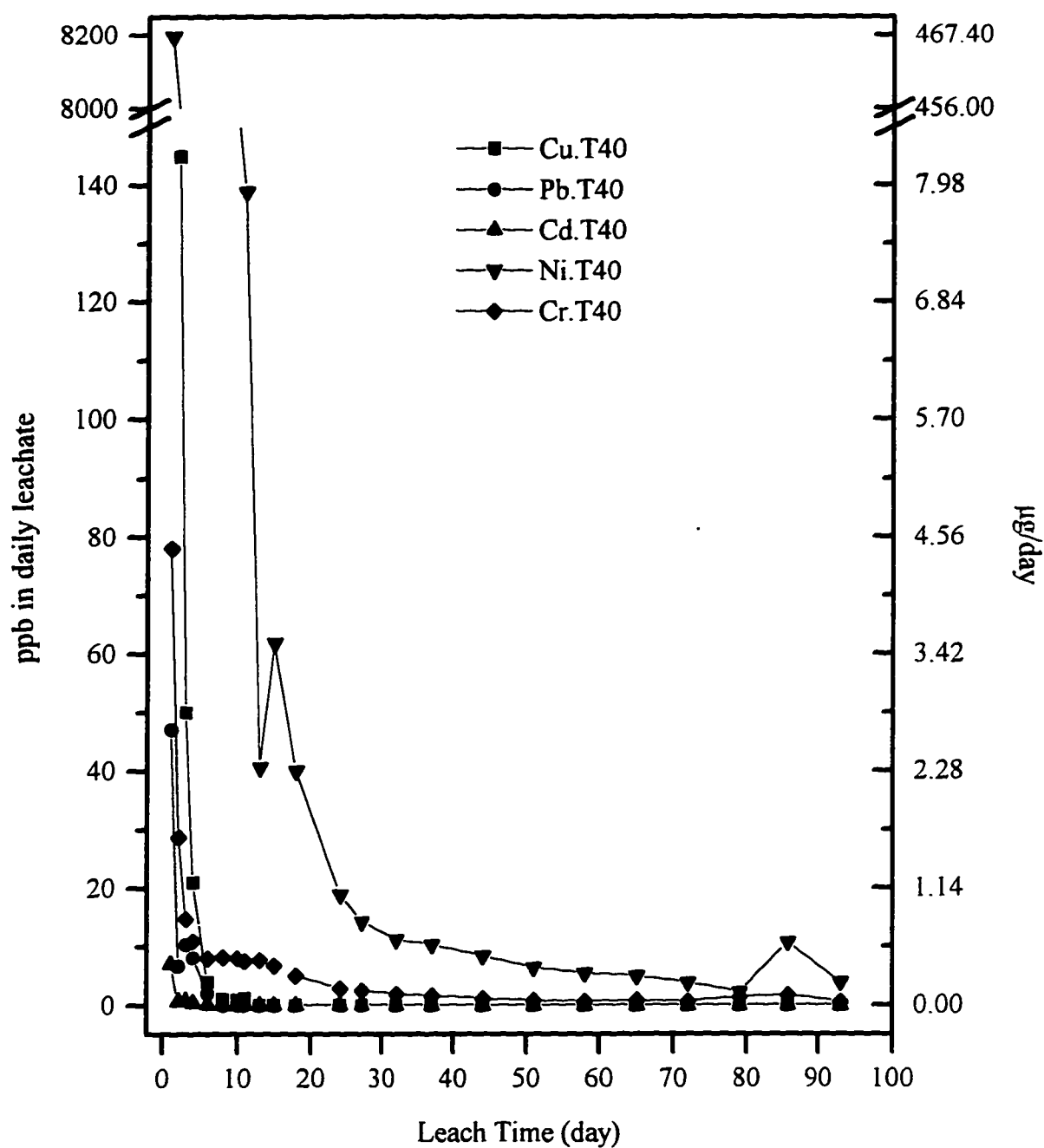


Figure 4.15 Heavy metal leaching profiles of thermally-dried sludge using pH 4.0 leaching solution.

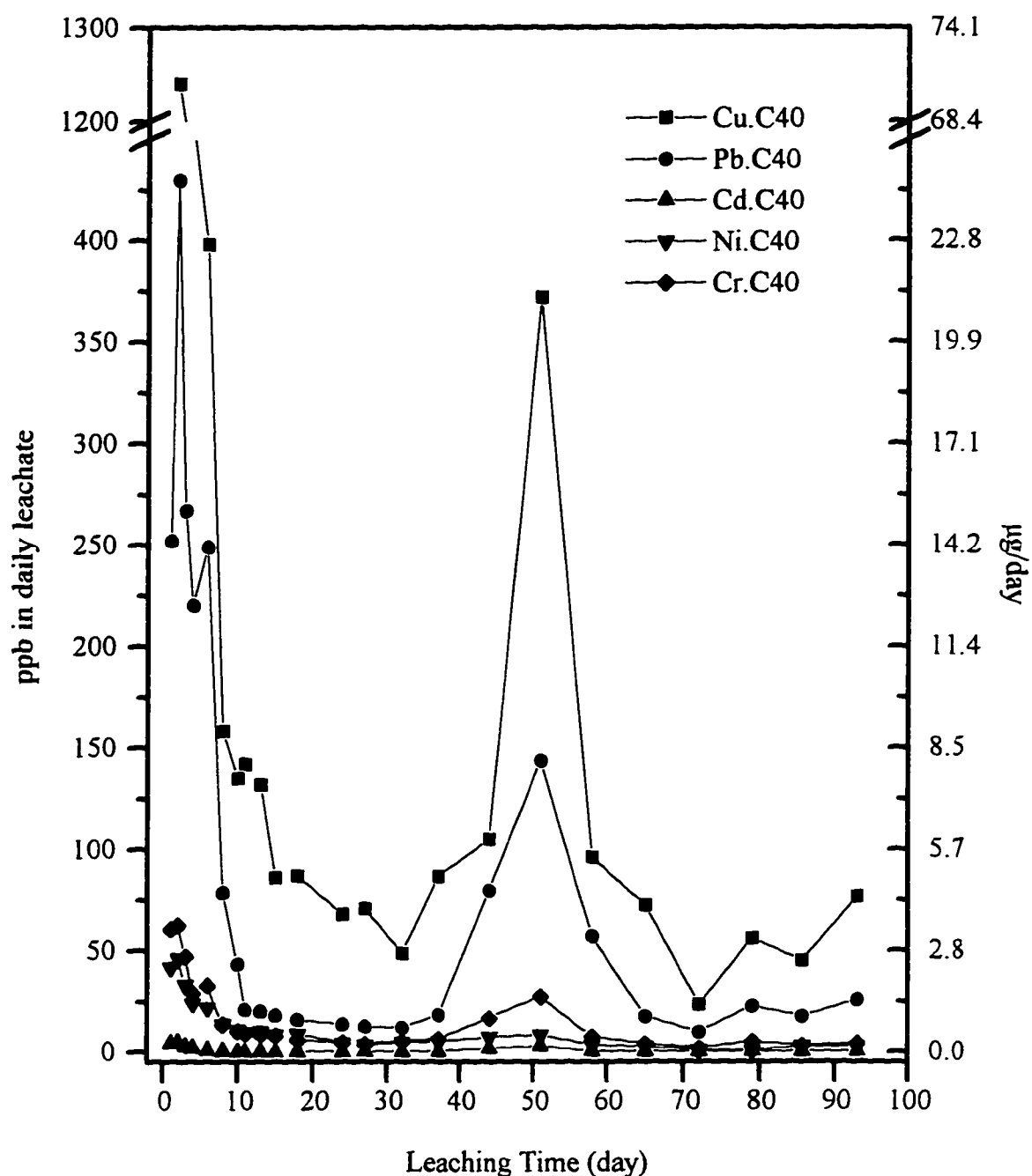


Figure 4.16 Metal leaching profiles of composted sludge using pH 4.0 leaching solution

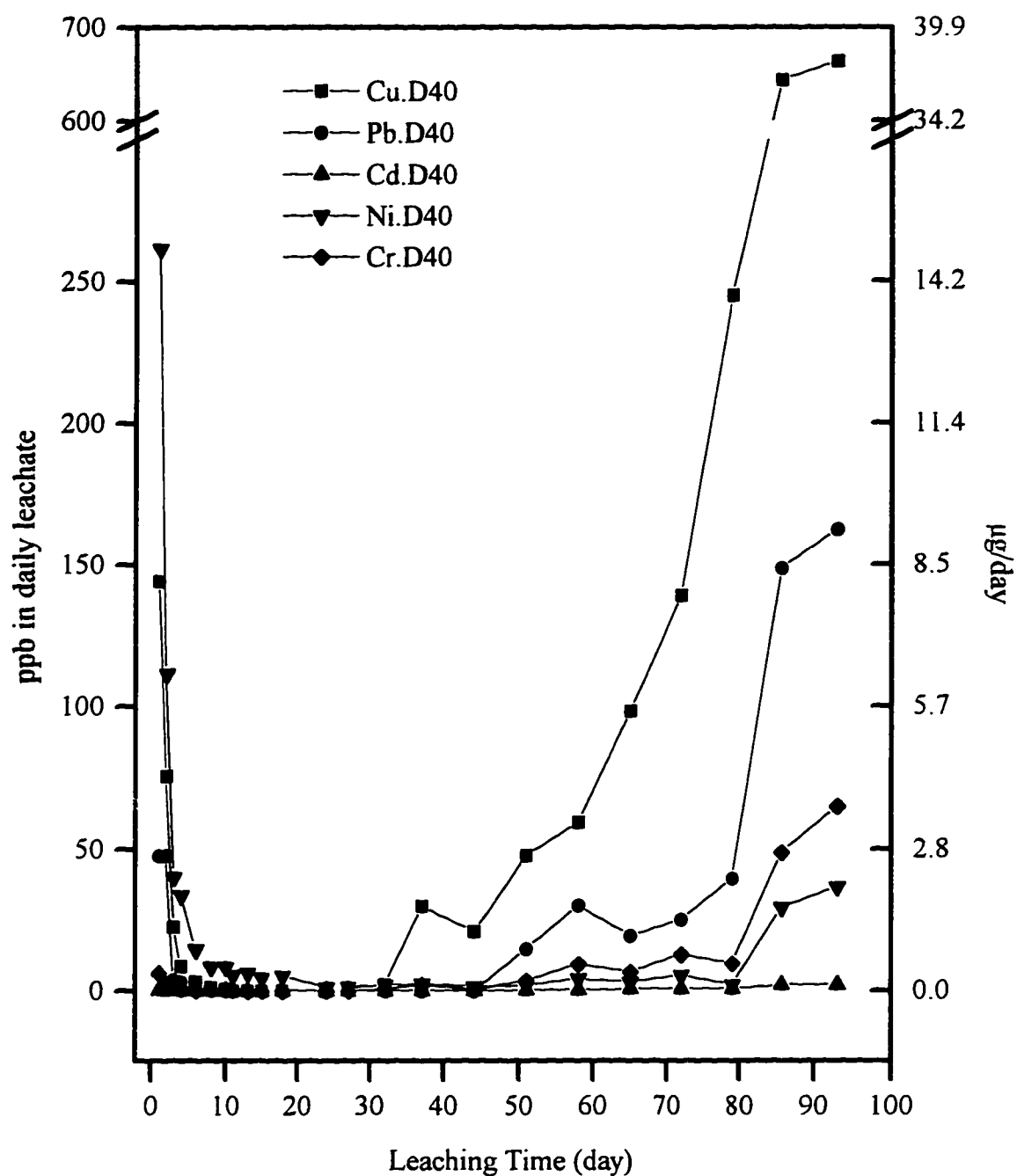


Figure 4.17 Heavy metal leaching profiles of dewatered sludge using pH 4.0 leaching solution

previous studies [92-94] have been conducted on anaerobically digested sludges and on a limited number of metals. Untreated sludges have a substantial complexing capacity which could be expected to be utilized by most heavy metals. Worthington [6] found that the complexing capacity of sludge was modified by the type of sludge treatment given. The thermal drying process destroys most organic complexing agents and leaves the metals in oxide, carbonate and sulfide forms [24]. Therefore metal complexes in dewatered and composted sludges are more leachable than in thermally-dried sludge. Thomas et al. [90] also have shown that the largest percentage of Al, Cd, and Pb were extracted from the organic fraction, or pyrophosphate-extractable phase, of the dewatered sludge. After thermal drying, the largest percentages of Al, Cd and Pb were found in oxalates, or amorphous oxides. Both Cd and Pb have been shown to exhibit a strong attraction to oxides of Al in aqueous solutions [95,96].

However, by comparison of the leaching profiles of net composted sludge and dewatered sludge in Figure 4.16 and Figure 4.17, it is seen that the leaching time in Figure 4.17 may be not long enough to show the highest concentrations of heavy metals in dewatered sludge. It was observed visually that the dewatered sludge appeared not to be penetrated by the leaching solution until about 60 days. Before 60 days only small amounts of metals were leached. After the sludge was completely soaked by aqueous solution (after 60 days) an substantial amount of metals was leached, but the maximum concentrations of heavy metals were still not reached by the end of this leaching period

(93 days in Figure 4.17). Using a longer leaching time, the total percentage of metal leached in dewatered sludge is expected to be larger than that in composted sludge based on the leaching profiles. A direct comparison is made in Figure 4.18 on composted and dewatered sludge leaching profiles for Pb leached. The cumulative percentages leached are also plotted. After 90 days of leaching, the total percentage of Pb leached from the dewatered sludge catches up with or exceeds that from the composted sludge. In practice, the sludge is not exposed to wet conditions the whole time. Both nutrients and toxic matter in dewatered sludge are not available to plants and ground water if it is not wetted by water more than 2 months because of its poor permeability to water. As a result, the dewatered sludge may be much more suitable for surface disposal, .e.g. monofill, waste pile in an environmentally safe manner, than for agricultural land application, where either nutrients are unavailable, or available together with toxic heavy metals in wet land application. This material was not mixed with soil and leached in this research since it was believed that this was not the intended use of the dewatered sludge by the DEP.

The characteristic behavior of the peak in leaching profiles of Pb and Cu from neat composted sludge suggests a rather non-uniform distribution of major and minor elements both on the surface and as a function of depth in the sludge.

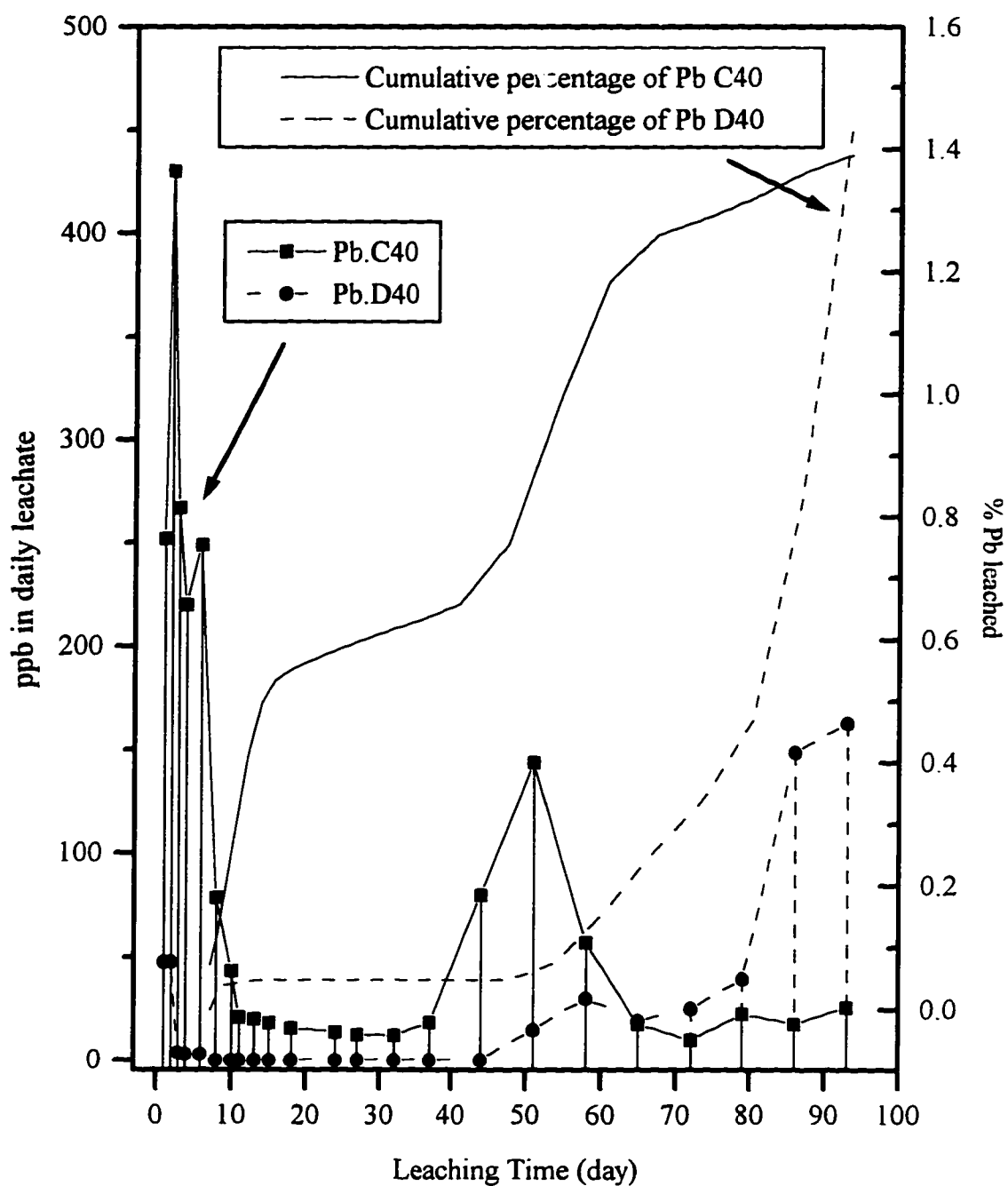


Figure 4.18 Integrations of heavy metal Pb leached from composted and dewatered sludges using pH 4.0 leaching solution.

4.7.6 Net Soil Leaching

Based on the leaching results of LI soil and Brooklyn soil, if certain percentages of heavy metals were leached in a 3 month period, the question arises as to why there are any heavy metals left in the soil since soils have been leached by precipitation over ten thousand years or so. There are two main natural processes to account for this concern: 1). there is continuously deposition of heavy metals from the atmosphere to replace the metal leached [97,98], and 2). it is thought that exposure to weathering , with repeated wetting-drying cycles and freeze-thaw cycles may have a large impact on the location of the metal ion in the soil matrix, type of bonding, and valence of the metal ion. In arid climate seasons, net water movement in the soil profile is upward, and the mobile elements that are carried to the surface become concentrated by evaporation. Conversely, in wet climate seasons, mobile elements leach downward as long as there is free drainage [99].

Figure 4.19 to Figure 4.20 show some heavy metal leaching profiles from the LI and Brooklyn soils. The leaching profiles from both soils are similar with the initial spikes in Fe, Ni, Pb, and Cu. The metal concentrations in Brooklyn soil are found substantially higher than those in LI soil although they are well below the maximum contaminant level promulgated under the Safe Drinking Water Act listed in Table 4.7. Given the facts that the total amount of heavy metal contents in LI soil is very low, and LI soil itself is coarse-textured, sandy and gravel loam, the small amount of metals only in soluble forms are quickly run off by leaching solution from the soil surface, e.g. Pb and Fe in Figure 4.21 and

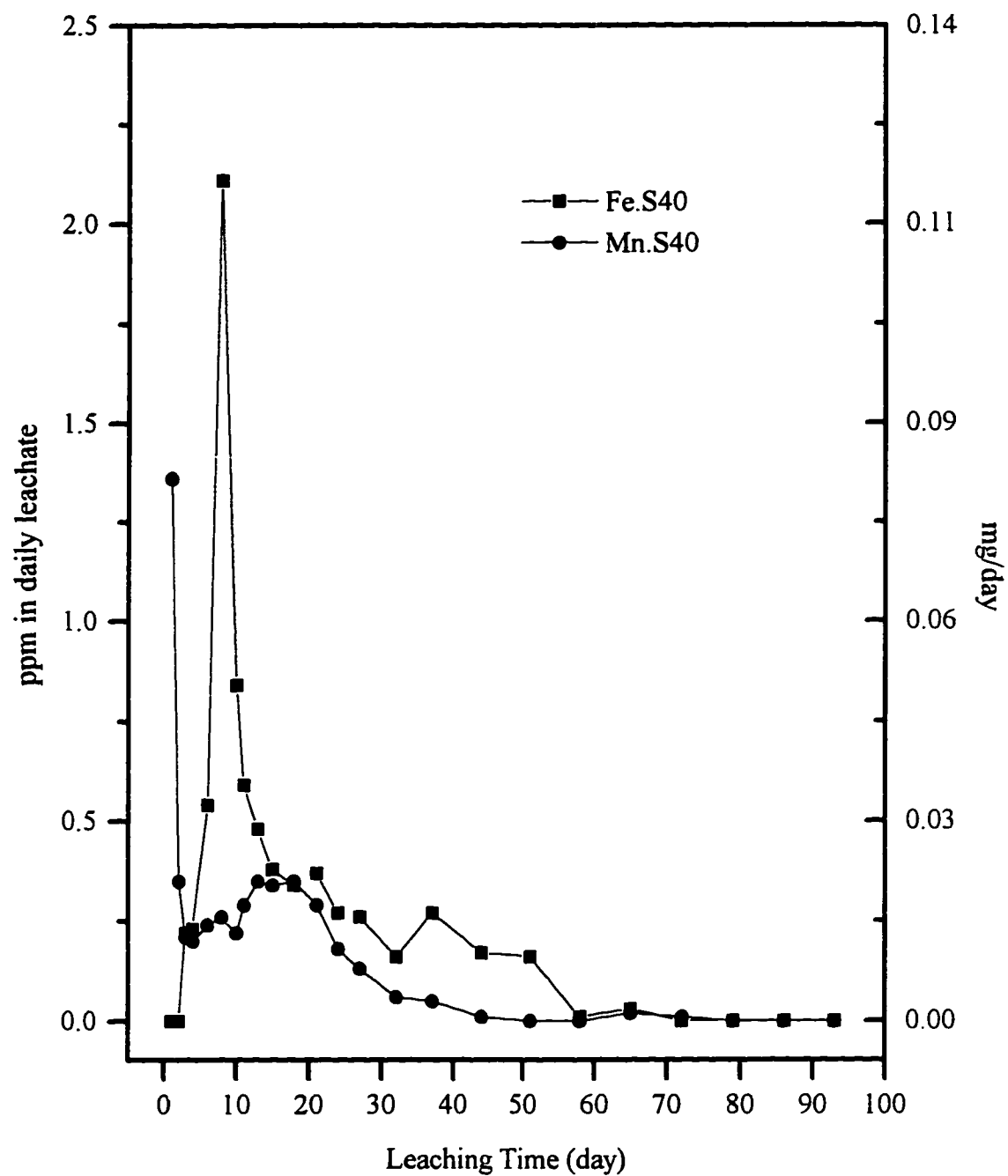


Figure 4.19 Leaching profiles of Fe and Mn from neat LI soil using pH 4.0 solution

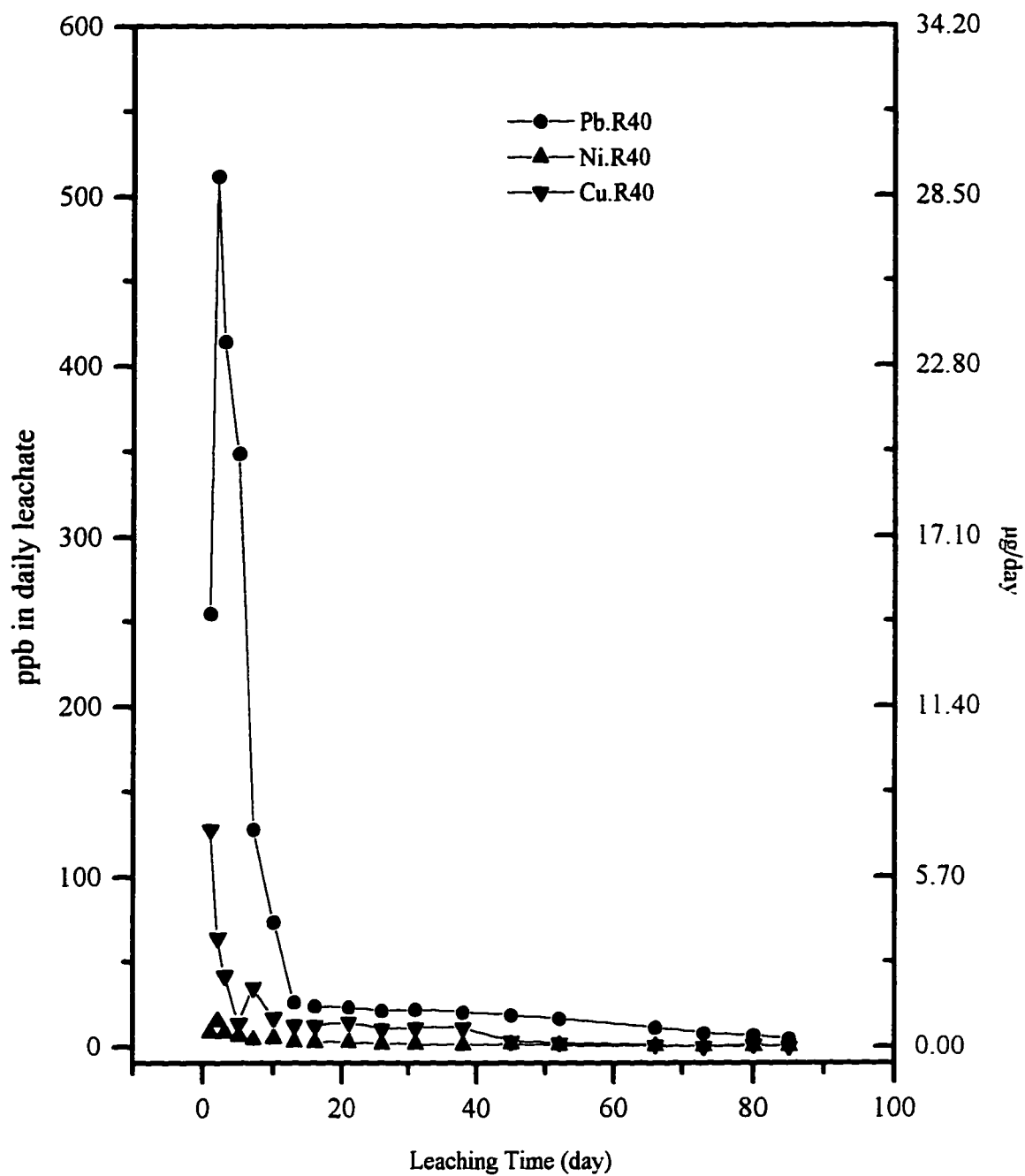


Figure 4.20 Leaching profiles of Cu, Pb, and Ni from neat Brooklyn soil using pH 4.0 solution

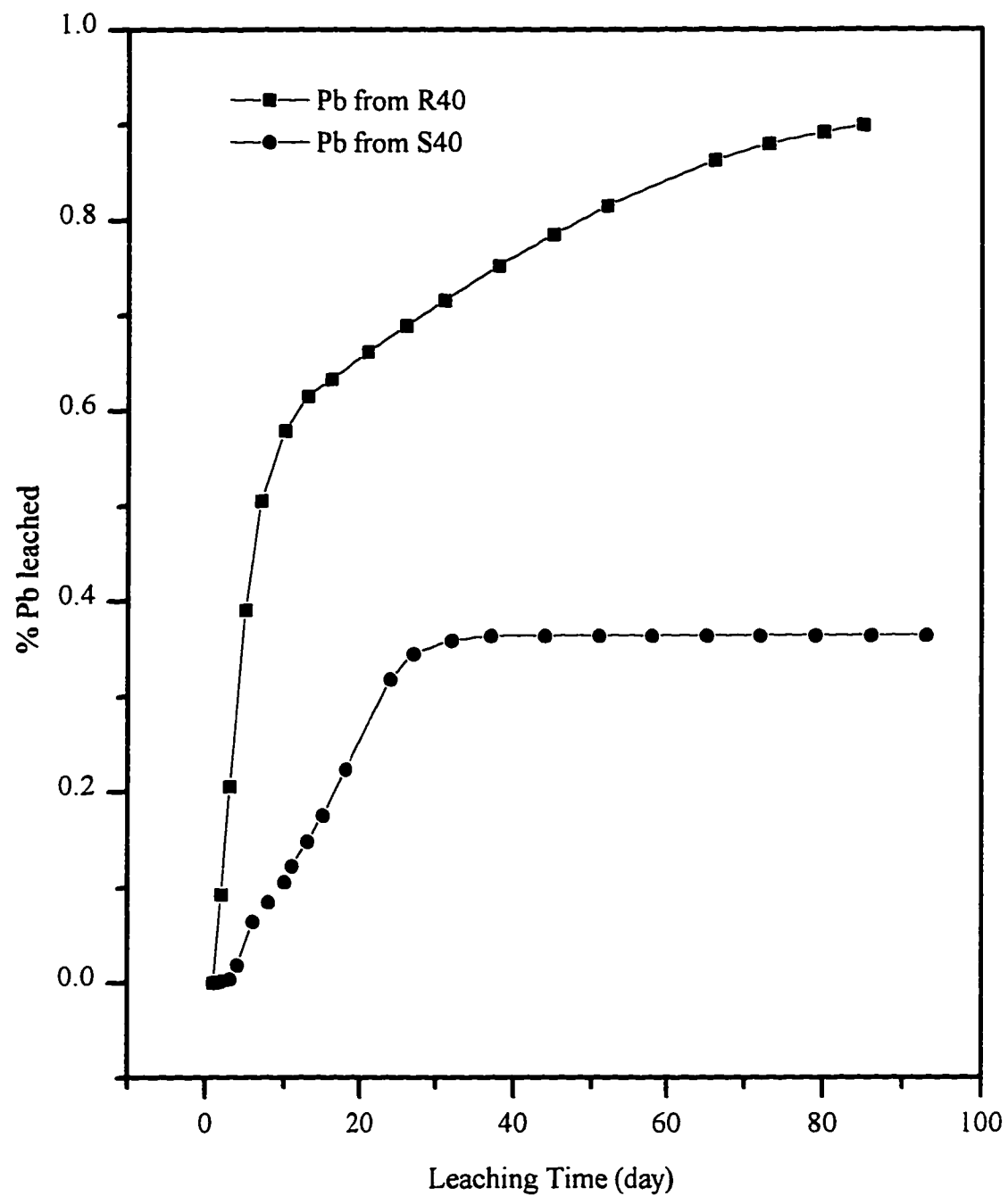


Figure 4.21 Percentages of Pb leached from LI and Brooklyn soils using pH 4.0 solution

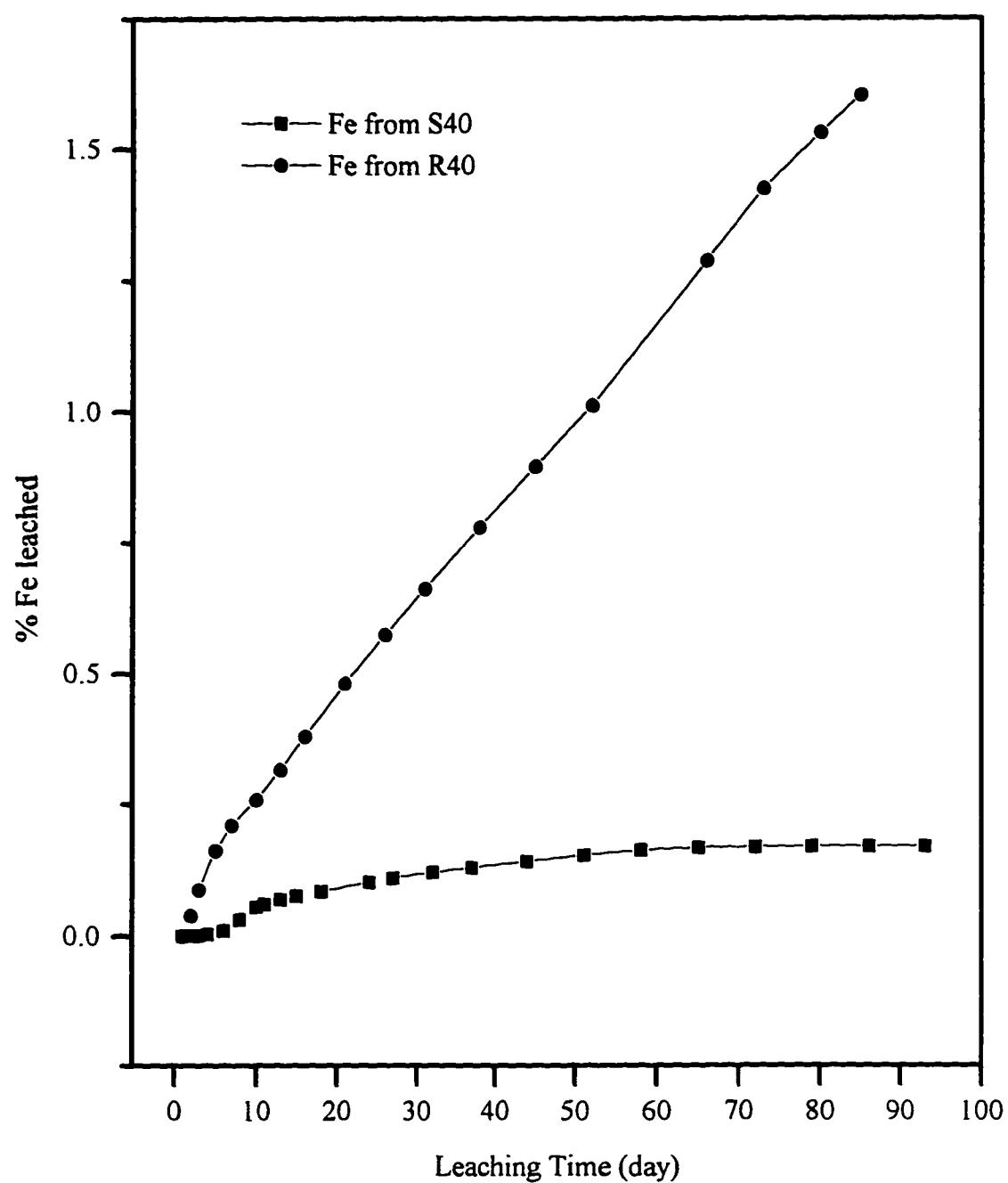


Figure 4.22 Percentages of Fe leached from LI and Brooklyn soils using pH 4.0 solution

4.22. The residual consists of silicates and some other resistant minerals which may hold trace metals in their crystal structure. Metals bound to this fraction are not considered to create a phytoavailable pool since they are not expected to be solubilized over a reasonable period of time under natural conditions [100]. Conversely, Brooklyn soil contains generally higher concentrations of metals to begin with, but also more organic and humic matter (see Table 4.3). After soluble, weakly hydrating cations such as Pb and Zn are quickly leached over a 10-day period (Figure 4.21 and 4.22), the rate of heavy metals leached from Brooklyn soil slows down and becomes constant. This part of the leaching profile may represent the most heavy metals exchangeable and somewhat mobile in Brooklyn soil which is determined by the leachability of its exchangeable sites with large molecular-weight humic materials which are constantly dissolving in the leaching solution [101].

4.7.7 Leaching of sludge products mixed with soil

The addition of sludge to soil alters the leaching profile of heavy metals. This will be a function of not just the migration of metal species, but also of physical incorporation during cultivation. In addition to concern about metals being available to plants through leaching into the soil solution, land application of sludge may lead to ground and surface water contamination by heavy metals. It is difficult to predict this because it depends strongly on the hydrological features of a site. Tables 4.8 to 4.11 summarize the concentrations of 11 heavy metals in daily leachates from 2 sludge products applied to 2 types of soils.

Concentrations of As, Cd, Cr, Pb, and Se leached are below the maximum contaminant level promulgated under the Safe Drinking Water Act listed in Table 4.7.

Table 4.7 Maximum contaminant levels (MCLs) promulgated under the Safe Drinking Water Act [40 CFR 257]

<u>Heavy metal</u>	<u>MCL (ppm)</u>
As	0.05
Cd	0.015
Cr	0.05
Pb	0.05
Se	0.01

Table 4.8 Metal concentrations in daily leachates from composted sludge mixed with Brooklyn soil leached with pH 4.0 solution

Smpl #	Day	ppb								ppm		
		As	Cd	Cr	Cu	Mo	Ni	Pb	Se	Fe	Mn	Zn
01CR40	1	2.52	1.25	15.99	140.00	0.87	13.35	364.33	0	4.51	0.08	1.03
02CR40	2	4.06	3.94	28.89	344.00	2.68	21.56	490.80	0	9.17	0.16	1.22
03CR40	3	4.93	1.20	18.44	48.00	5.87	13.05	366.60	0	4.96	0.10	0.80
04CR40	5	4.26	0.63	12.94	40.00	2.17	7.96	271.33	0	3.59	0.15	0.70
05CR40	7	3.98	0.20	7.10	25.80	2.45	7.43	123.00	0	1.71	0.21	0.57
06CR40	10	2.93	0.12	5.22	19.80	1.98	6.04	88.88	0.78	2.01	0.32	0.40
07CR40	13	1.96	0.10	4.22	21.50	1.78	2.82	25.44	0	2.26	0.29	0.41
08CR40	16	2.19	0.08	3.82	18.20	1.7	3.08	24.18	0	2.69	0.32	0.30
09CR40	21	1.74	0.09	2.91	21.70	1.59	2.50	23.93	0	2.30	0.25	0.29
10CR40	26	1.33	0.14	2.68	18.70	1.5	1.32	23.81	0	2.44	0.26	0.24
11CR40	31	1.11	0.16	2.29	20.90	0.82	1.45	24.19	0	2.39	0.25	0.14
12CR40	38	0.95	0.14	1.57	24.50	0.32	0.95	26.07	0	2.80	0.33	0.56
13CR40	45	0.80	0.09	1.07	5.90	0.15	1.27	25.53	0	2.74	0.34	0.48
14CR40	52	0.39	0.09	0.71	5.70	0.08	1.23	22.92	0	2.99	0.33	0.48
15CR40	66	0.13	0.00	0.30	2.30	0.03	1.30	15.44	0	3.95	0.46	0.25
16CR40	73	0.06	0.00	0.25	0.80	0	0.00	11.23	0	2.55	0.29	0.31
17CR40	80	0.03	0.00	0.22	0.00	0	0.00	7.60	0	2.36	0.26	0.23
18CR40	85	0.02	0.00	0.21	0.00	0	0.00	4.59	0	2.46	0.27	0.19

Table 4.9 Metal concentrations in daily leachates from themally dried sludge mixed with Brooklyn soil leached with pH 4.0 solution

Smpl #	day	ppb								ppm		
		As	Cd	Cr	Cu	Mo	Ni	Pb	Se	Fe	Mn	Zn
01TR40	1	2.31	3.20	16.60	246.67	1.32	60.93	43.80	0.65	4.66	0.12	1.39
02TR40	2	4.27	1.34	17.67	138.00	9.25	40.75	432.80	0	5.73	0.14	0.97
03TR40	3	4.90	0.72	12.00	172.00	5.4	23.76	340.80	0	3.56	0.14	0.78
04TR40	5	5.89	0.74	8.51	70.00	1.83	20.62	237.60	0	2.71	0.25	0.71
05TR40	7	6.25	0.21	3.16	33.70	6.35	20.37	70.00	0	1.19	0.47	0.45
06TR40	10	5.82	0.24	2.57	25.10	2.05	10.30	53.65	0	1.65	0.44	0.66
07TR40	13	4.32	0.25	1.94	20.50	1.82	6.80	25.27	0	1.81	0.38	0.47
08TR40	16	2.97	0.19	1.62	11.20	1.47	3.92	23.26	0	2.17	0.42	0.38
09TR40	21	2.50	0.32	1.29	11.30	1.04	1.68	25.45	0	2.11	0.35	0.38
10TR40	26	2.18	0.31	1.18	9.50	1.11	1.85	25.38	0	2.33	0.36	0.34
11TR40	31	1.65	0.32	1.03	15.60	0.74	1.97	25.26	0	2.32	0.35	0.24
12TR40	38	1.36	0.33	0.86	7.90	0.53	1.10	24.99	0	2.34	0.36	0.63
13TR40	45	0.96	0.26	0.60	5.00	0.31	1.12	23.92	0	2.49	0.37	0.54
14TR40	52	0.68	0.23	0.67	4.50	0.09	0.65	21.27	0	2.49	0.34	0.51
15TR40	66	0.32	0.00	0.29	2.20	0.02	0.05	14.94	0	3.22	0.21	0.40
16TR40	73	0.15	0.00	0.24	6.80	0.02	0.00	12.70	0	2.34	0.31	0.32
17TR40	80	0.08	0.00	0.10	1.60	0	0.00	10.02	0	2.25	0.28	0.22
18TR40	85	0.04	0.00	0.13	0.00	0	0.00	8.71	0	2.46	0.30	0.11

Table 4.10 Metal concentrations in daily leachates from composted sludge mixed with LI soil leached with pH 4.0 solution

Smpl #	day	ppb								ppm		
		As	Cd	Cr	Cu	Mo	Ni	Pb	Se	Fe	Mn	Zn
01CS40	1	0.29	0.48	0.47	7.50	0	3.47	8.91	2.52	0.06	1.54	0.71
02CS40	2	0.32	0.10	0.88	10.00	0	1.48	9.60	0	1.14	0.35	0.55
03CS40	3	0.34	0.14	4.58	19.30	0.21	1.51	27.22	0	2.06	0.28	0.45
04CS40	5	0.40	0.13	6.90	17.50	0	1.62	29.43	0	4.28	0.39	0.35
05CS40	7	0.45	0.07	10.25	22.80	0	1.42	27.54	0.12	2.23	0.66	0.51
06CS40	10	0.35	0.06	4.77	9.90	0	0.98	18.53	0.75	2.68	0.87	0.44
07CS40	13	0.30	0.05	4.64	31.10	0.64	0.01	16.60	0	2.65	0.85	0.38
08CS40	16	0.21	0.01	2.05	2.60	0	0.00	9.42	0.51	2.63	0.84	0.31
09CS40	21	0.18	0.00	0.78	1.10	0.18	0.00	4.11	0.21	2.67	0.73	0.33
10CS40	26	0.14	0.00	0.79	0.40	0.48	0.00	2.94	0.04	3.19	0.71	0.29
11CS40	31	0.11	0.00	0.81	0.00	0.09	0.00	2.11	0	3.23	0.63	0.19
12CS40	38	0.07	0.00	0.55	0.60	0	0.00	1.59	0.13	2.97	0.48	0.43
13CS40	45	0.03	0.00	0.32	0.40	0	0.00	0.00	0.09	2.70	0.41	0.41
14CS40	52	0.01	0.00	0.21	1.10	0.02	0.00	0.00	0	2.24	0.33	0.49
15CS40	66	0.02	0.00	0.12	2.80	0	0.00	0.75	0	2.73	0.44	0.42
16CS40	73	0.10	0.00	0.17	9.50	0.51	0.00	21.51	0.27	1.46	0.24	0.73
17CS40	80	0.02	0.00	0.08	0.50	0	0.00	1.57	0	1.21	0.21	0.22
18CS40	85	0.01	0.00	0.05	2.40	0	0.00	0.87	0	1.22	0.22	0.18

Table 4.11 Metal concentrations in daily leachates from thermally dried sludge with LI soil leached with pH 4.0 solution

Smpl #	day	ppb								ppm		
		As	Cd	Cr	Cu	Pb	Mo	Ni	Se	Fe	Mn	Zn
01TS40	1	0.89	0.26	1.28	31.50	1.81	0.02	28.51	3.63	0.02	1.28	0.55
02TS40	2	0.33	0.05	1.75	25.40	5.50	0.02	25.01	0.87	0.38	0.53	0.63
03TS40	3	0.15	0.02	3.08	13.80	4.84	0.01	16.95	0.07	1.23	0.37	0.54
04TS40	5	0.07	0.03	1.43	3.50	4.87	0.00	14.58	0.44	0.75	0.76	0.32
05TS40	7	0.53	0.01	1.74	1.00	3.95	0.00	13.77	4.37	0.85	1.30	0.49
06TS40	10	0.51	0.02	1.56	2.90	8.38	0.00	5.56	0.61	1.25	0.94	0.37
07TS40	13	0.29	0.01	1.67	3.40	7.73	0.00	3.31	1.07	1.11	0.75	0.39
08TS40	16	0.32	0.00	1.17	0.70	6.89	0.00	1.67	0	1.29	0.83	0.43
09TS40	21	0.54	0.00	1.26	1.10	9.74	0.00	0.00	0	2.23	0.85	0.40
10TS40	26	0.41	0.00	0.80	0.80	9.74	0.00	0.08	0	3.62	1.01	0.23
11TS40	31	0.20	0.00	0.81	0.60	8.36	0.00	0.00	0	4.25	0.96	0.23
12TS40	38	0.09	0.00	0.72	0.50	5.47	0.00	0.00	0	4.19	0.68	0.68
13TS40	45	0.04	0.00	0.43	0.00	3.26	0.00	0.00	0	4.06	0.59	0.59
14TS40	52	0.02	0.00	0.31	0.60	1.22	0.00	0.00	0	3.87	0.50	0.45

4.7.7.1 Leaching of sewage sludge products mixed with LI soil

Figure 4.23 and Figure 4.24 show the leaching patterns of thermally dried sludge mixed with LI soil, and Figure 4.25 and Figure 4.26 show the leaching patterns of composted sludge mixed with LI soil. In the thermally dried sludge, Mn and Zn are present in trivial amounts in all the leachates. Fe in the leachate is closer to that in the neat thermally dried sludge. Ni and Pb show a sharp early spike; their concentrations in the mixture leachate are what be expected from the sludge component. Cu in leachate from the mixture (Figure 4.27) seems to reflect the thermally dried sludge behavior more than the soil.

In order to distinguish the interaction of soil and sludge, the leaching profiles from the neat sludge columns are multiplied by the ratio of the sludge loads in soil-sludge columns to the weight in the neat sludge column; these calculated profiles represent the neat sludge leaching profiles with same sludge weight used in sludge-soil columns. Also the calculated neat sludge profiles and neat soil profiles are added together to compare to the profiles from the soil-sludge columns (Figures 27 to 29).

The leaching profiles of Cu and Pb from composted sludge mixed with LI soil show that neat composted sludge (CS40) leaching characteristics dominates the whole leaching pattern of the mixture. This is shown by comparison of leaching profiles from calculated composted sludge (C40 calculated) for Cu in Figure 4.28 and Pb in Figure 4.29. The characteristic peak from the neat composted sludge

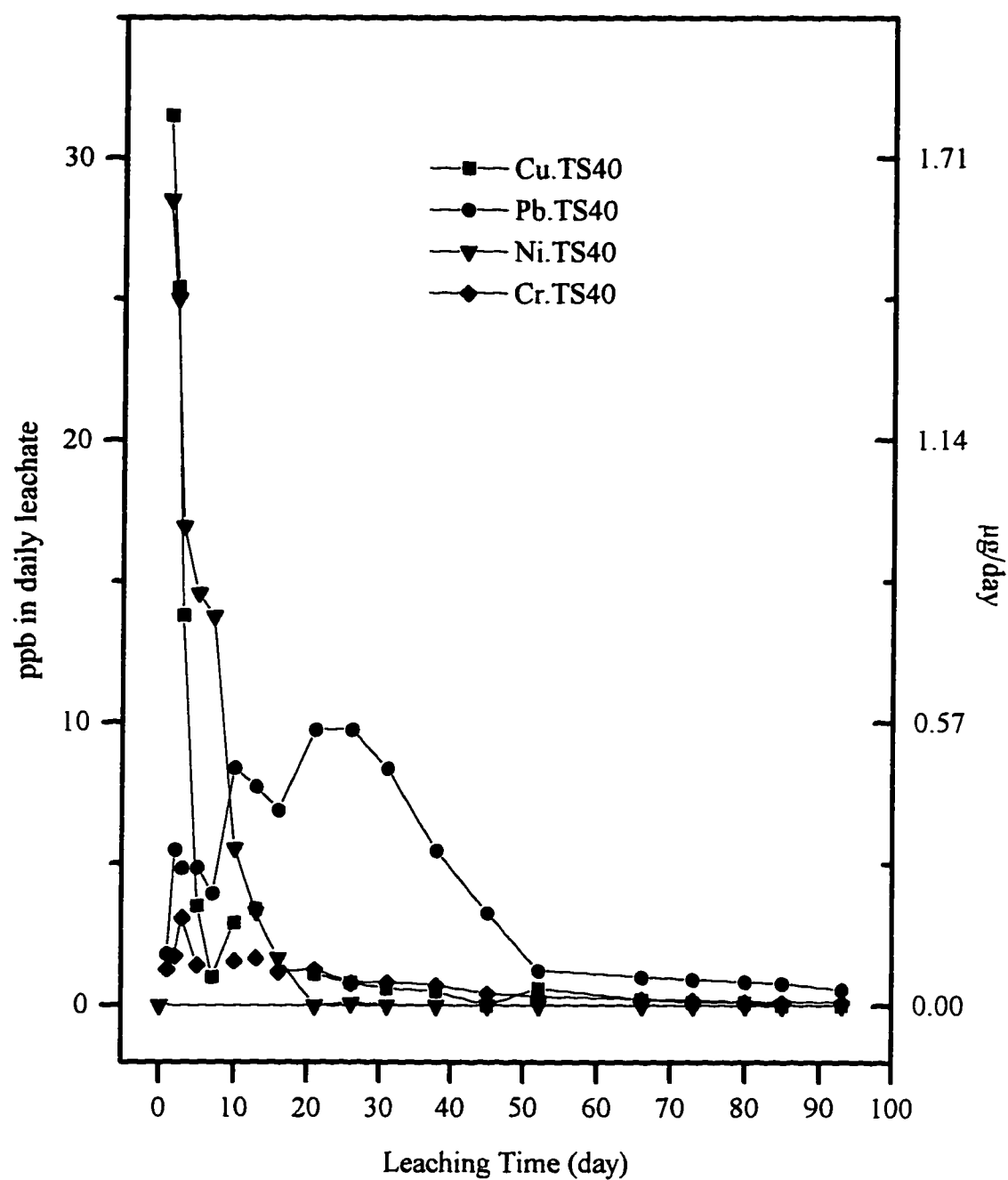


Figure 4.23 Leaching profiles of Cu, Pb, Ni and Cr from thermally dried sludge mixed with LI soil using pH 4.0 solution

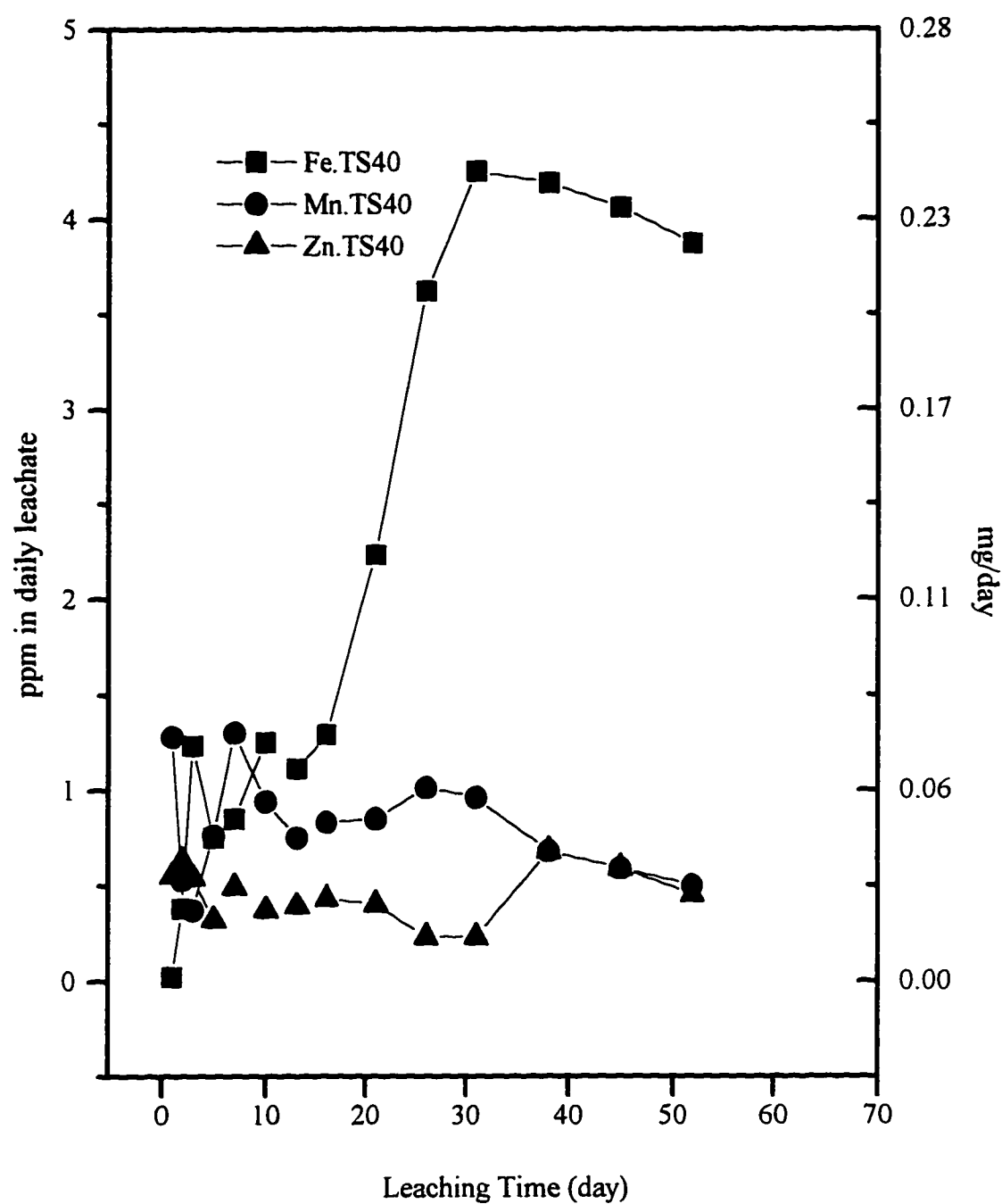


Figure 4.24 Leaching Profiles of Fe, Mn, Zn from thermally dried sludge mixed with LI soil using pH 4.0 solution

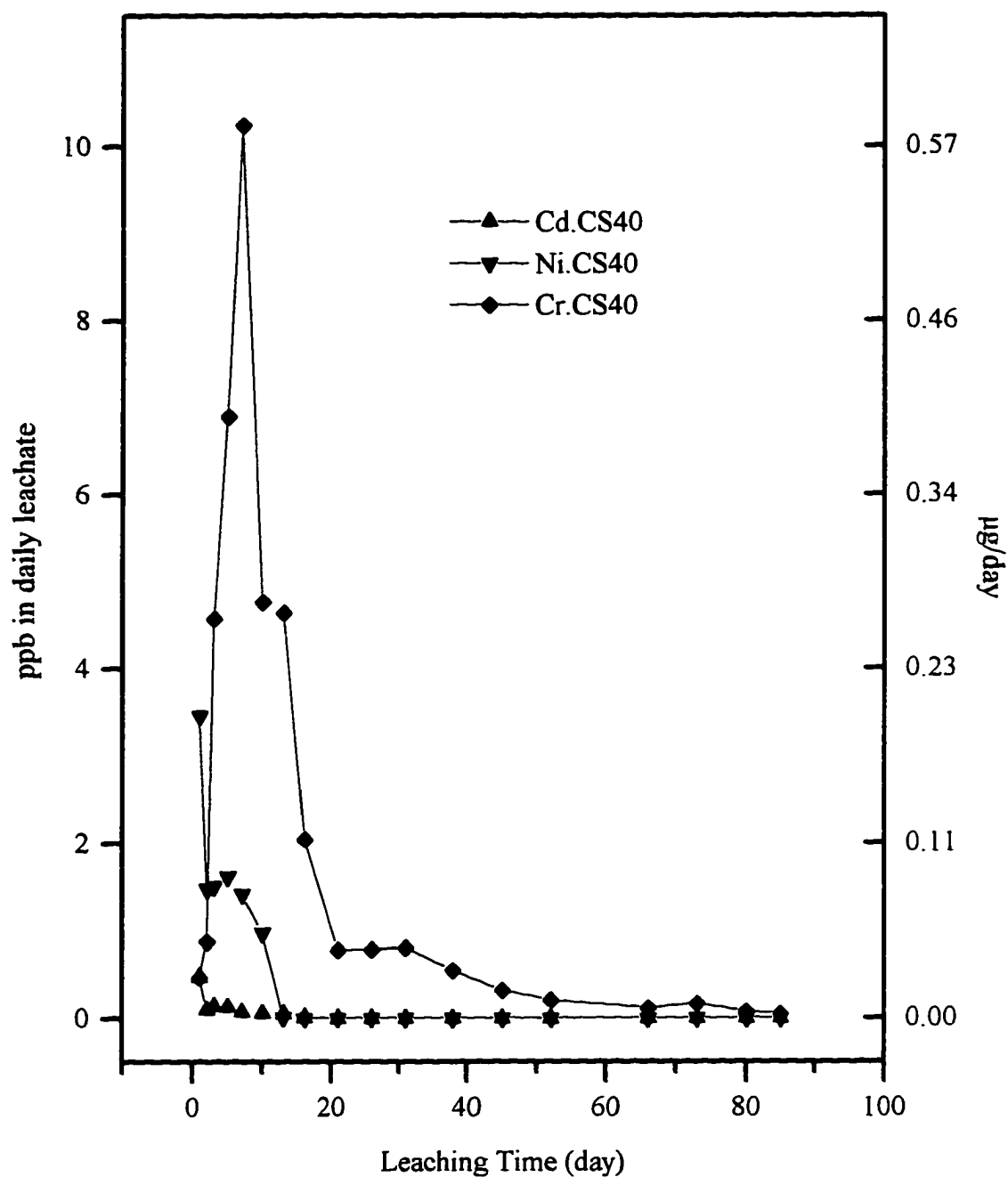


Figure 4.25 Leaching Profiles of composted sludge mixed with LI soil using pH 4.0 solution

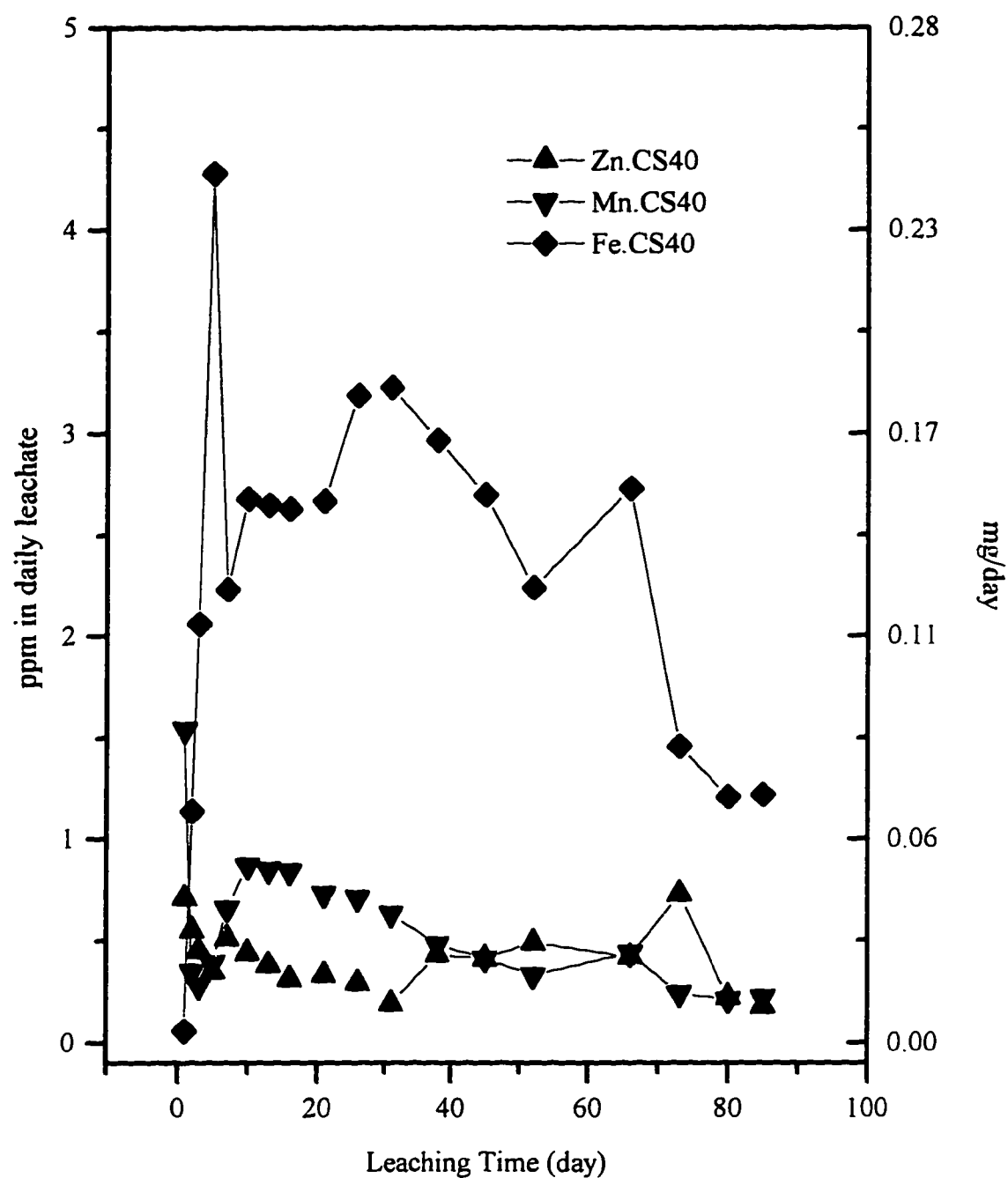


Figure 4.26 Leaching Profiles of Fe, Mn, Zn from composted sludge mixed with LI soil using pH 4.0 solution

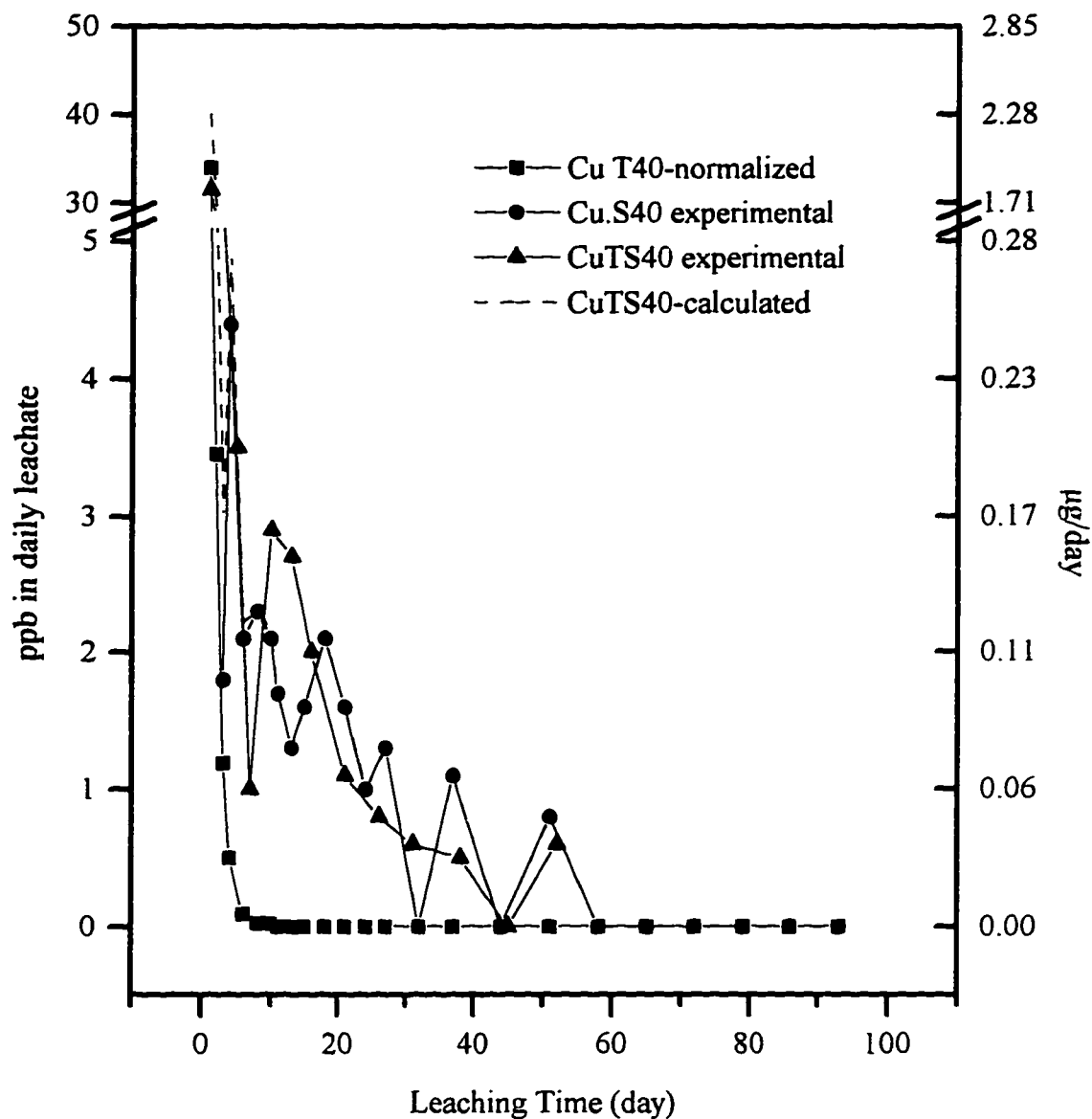


Figure 4.27 Leaching profiles of Cu from neat LI soil (S40), thermally dried sludge mixed with LI soil (TS40), and calculated Cu leaching profile.
 —■— Cu T40-normalized is neat T40 profile normalized to the sludge usage in the mixture. It is here equal to the neat T40 profile multiplied by the ratio of 1.19g/50g.
 - - TS40-calculated is the sum of neat soil leaching profiles —●— Cu S40 and —■— Cu T40 normalized.

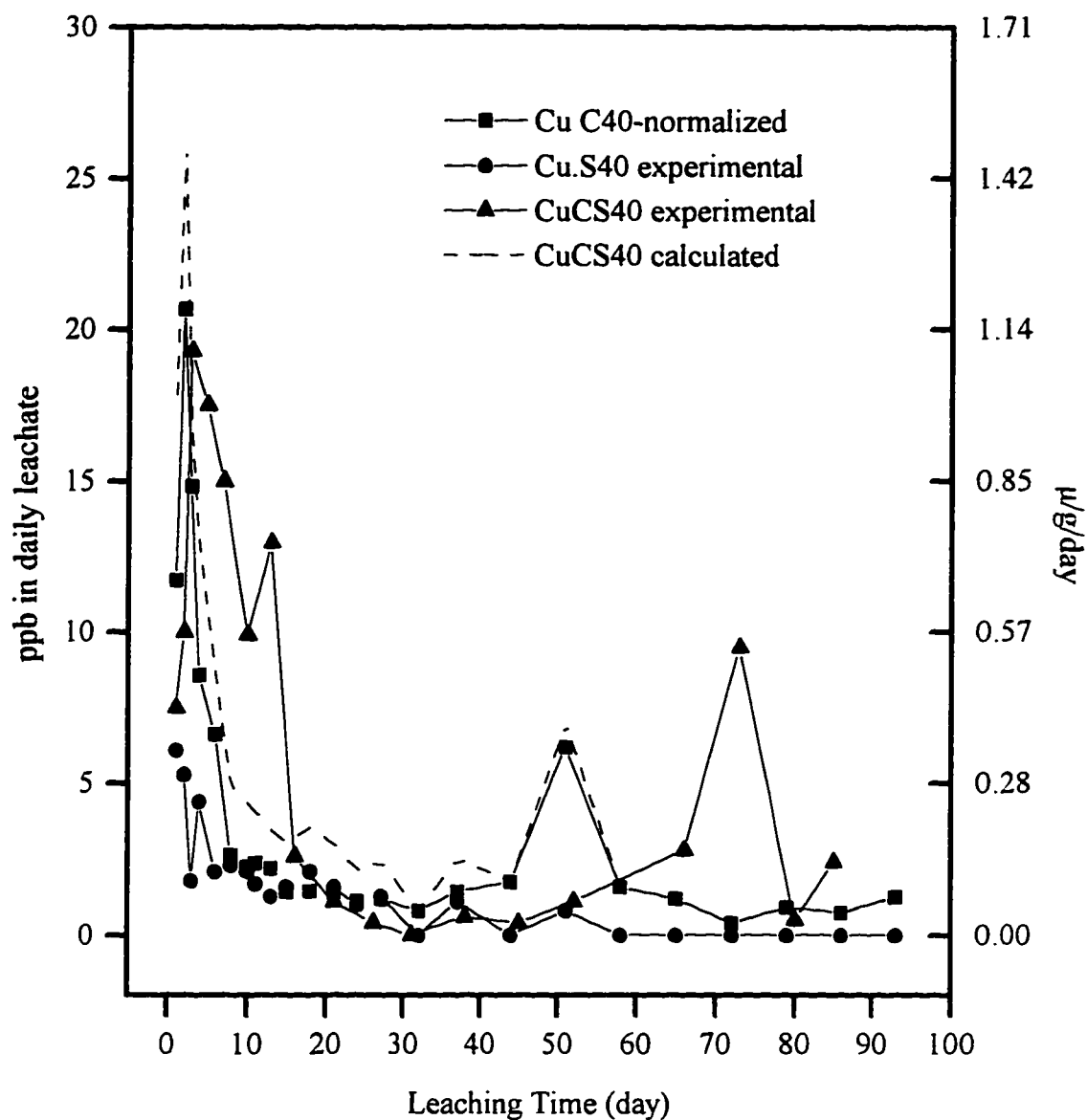


Figure 4.28 Leaching profiles of Cu from neat LI soil (S40), composted sludge mixed with LI soil (CS40), and calculated Cu leaching profile.

—■— Cu C40-normalized is neat C40 profile normalized to the sludge usage in the mixture. It is here equal to the neat C40 profile multiplied by the ratio of 2.02g/50g.

-- CS40-calculated is the sum of neat soil leaching profiles —●— Cu S40 and —■— Cu C40 normalized.

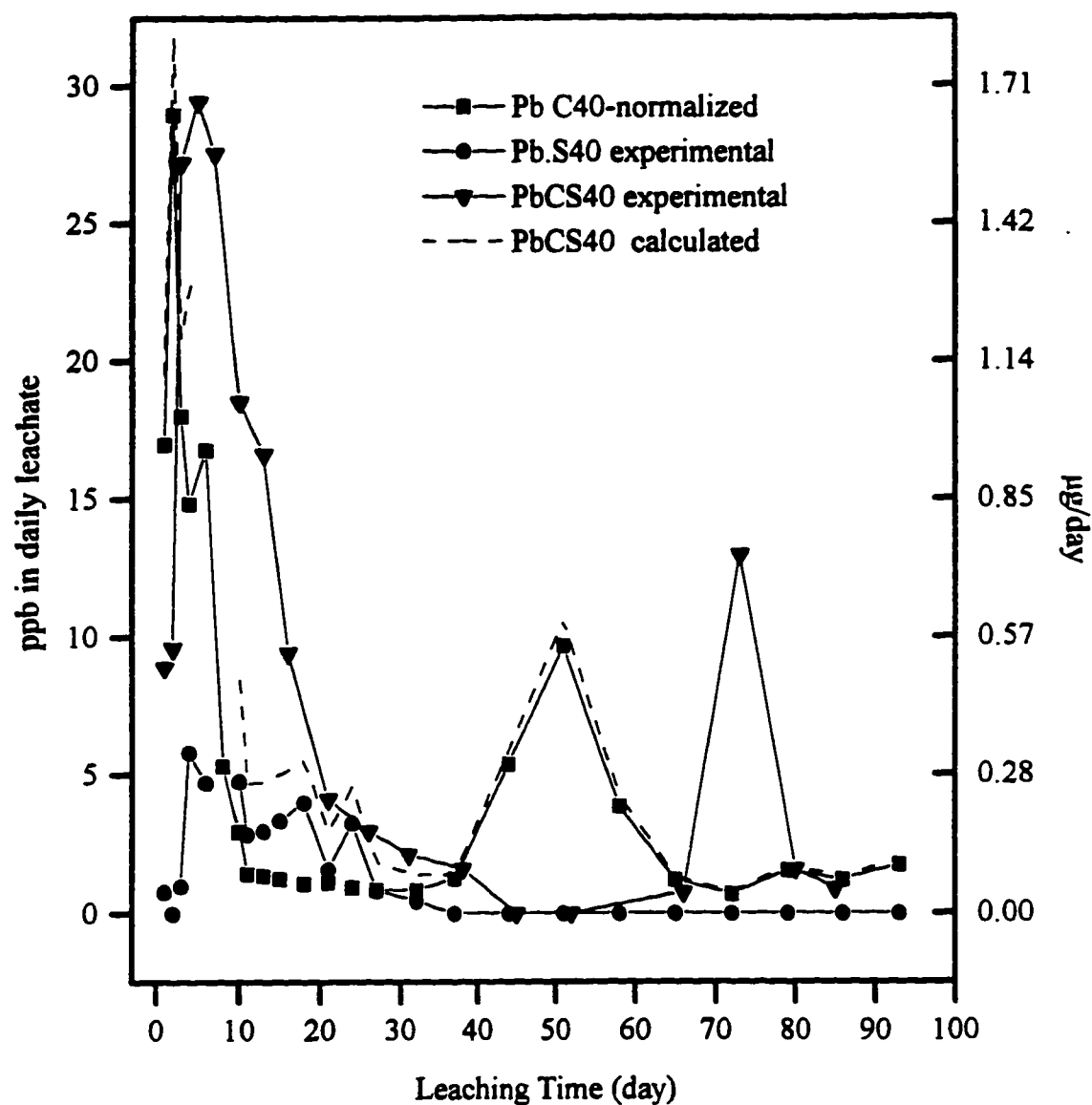


Figure 4.29 Leaching profiles of Pb from neat LI soil (S40), composted sludge mixed with LI soil (CS40), and calculated Pb leaching profile
 —■— Pb C40-normalized is the neat C40 profile normalized to the usage in the mixture. It is here equal to the neat C40 profile multiplied by the ratio 2.02g/50g.
 - - CS40-calculated is the sum of neat soil leaching profiles
 —●— Pb S40 and —■— Pb C40-normalized.

leaching profile remains in the leaching profile of the mixture with LI soil. The low concentration of heavy metals in LI soil (from Figure 4.9 to Figure 4.13) and the quick "run-off" of the metals in LI soil leaching profiles may indicate its low retentive capacity for heavy metals from the sludge, although the leaching characteristic peaks of compost sludges are delayed in the sludge-soil mixture because the metals have to travel through the soil. Heavy metals other than Fe, Mn, Zn, Cu and Pb from neat composted sludge together with all metals from thermally dried sludge did not show very high concentrations in leachates. Therefore their characteristics from the neat sludge leaching were not significant when the sludge products were mixed with LI soil.

4.7.7.2 Leaching of sewage sludge product mixed with Brooklyn soil

Comparison of Figure 4.20 for neat Brooklyn soil (R40) and Figures 4.30 to 4.33 for sludge -Brooklyn soil (CR40 and TR40) mixtures shows the leaching patterns for all metals from the mixtures are practically identical to those of the neat Brooklyn soil, especially for the thermally dried sludge whose contribution is negligible. Figures 4.34 and 4.35 show good agreement for Pb and Cu of TR40 calculated (dashed lines) with TR40 experimental. The dashed lines in the figures are calculated from the simple superposition of leaching profiles from neat soil and neat sludge ratioed to the load in the sludge-soil columns. Even with sandy soil, thermally dried sludge products contribute very

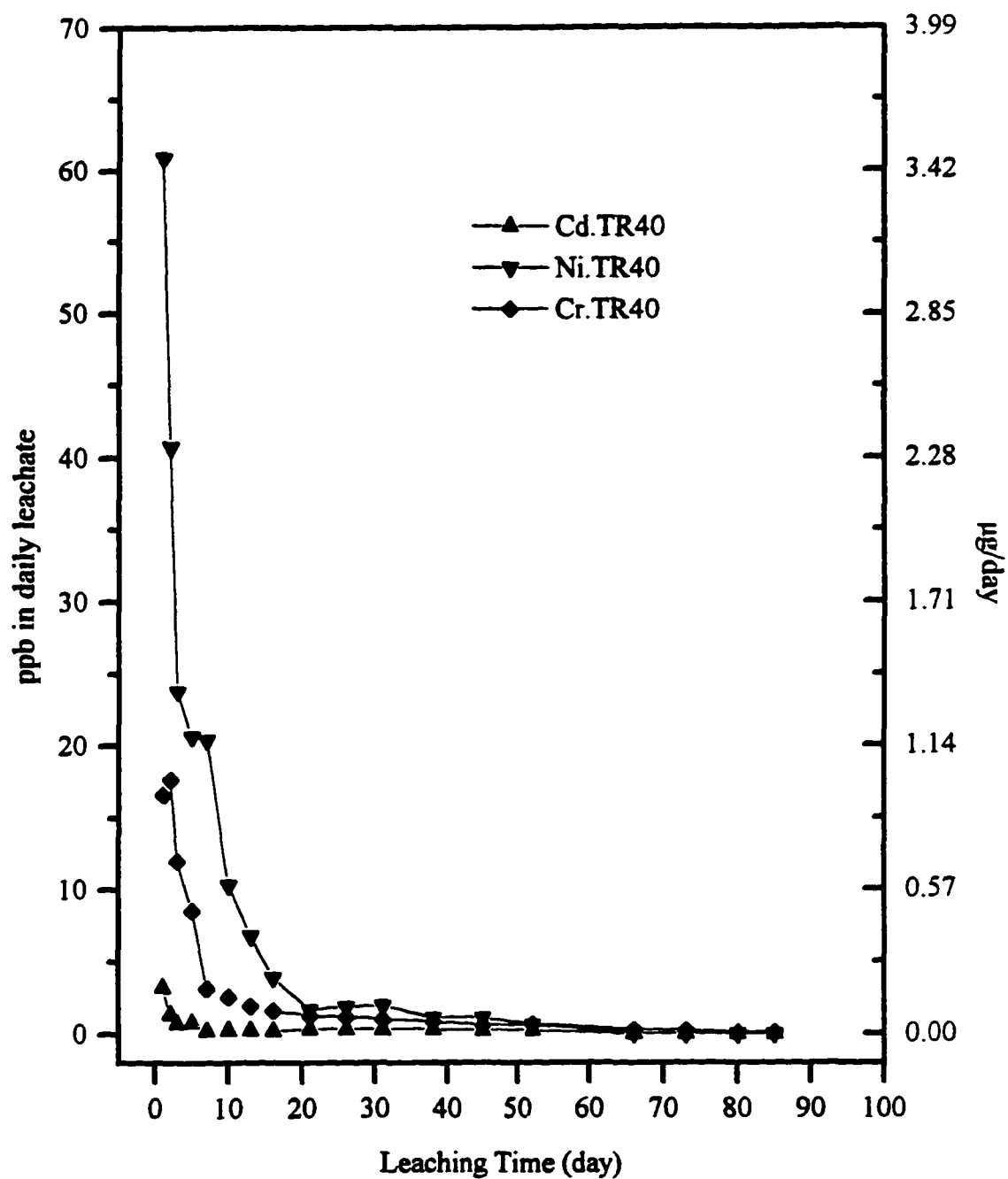


Figure 4.30 Leaching profiles of Cd, Ni and Cr from thermally dried sludge mixed with Brooklyn soil leached using pH 4.0 solution

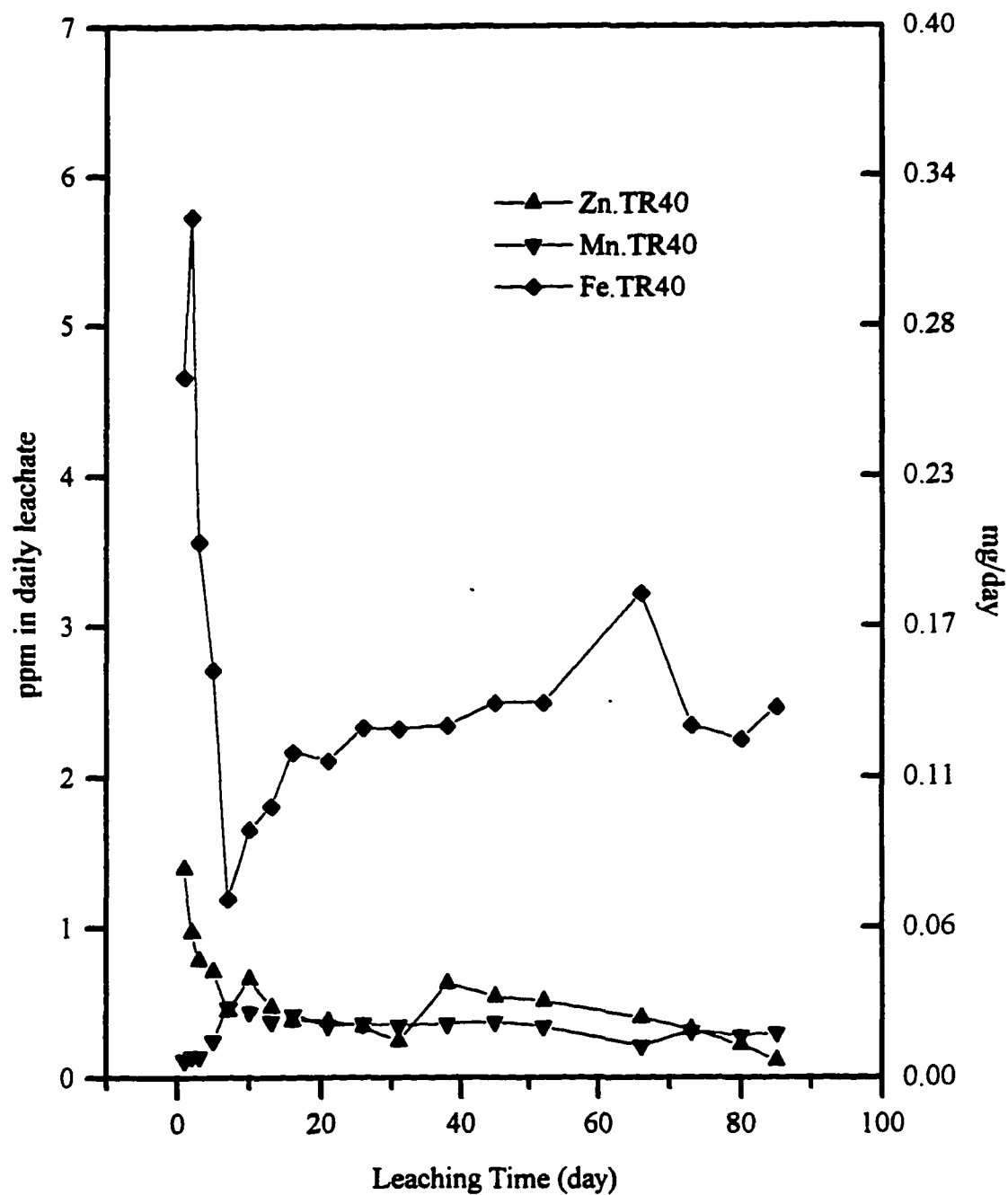


Figure 4.31 Leaching Profiles of Fe, Mn, Zn from thermally dried sludge mixed with Brooklyn soil leached using pH 4.0 solution

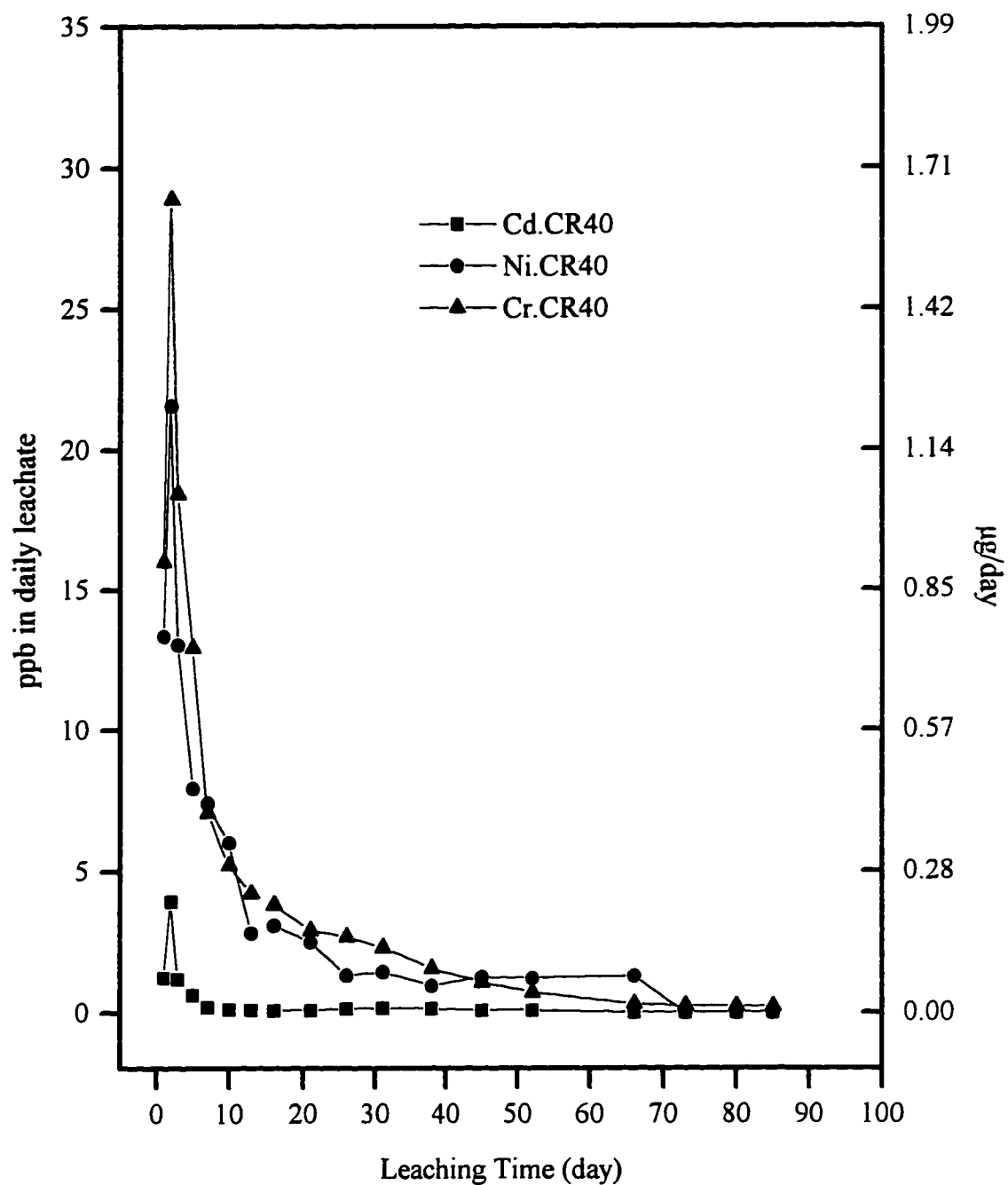


Figure 4.32 Leaching profiles of Cd, Ni, Cr from composted sludge mixed with Brooklyn soil using pH 4.0 solution

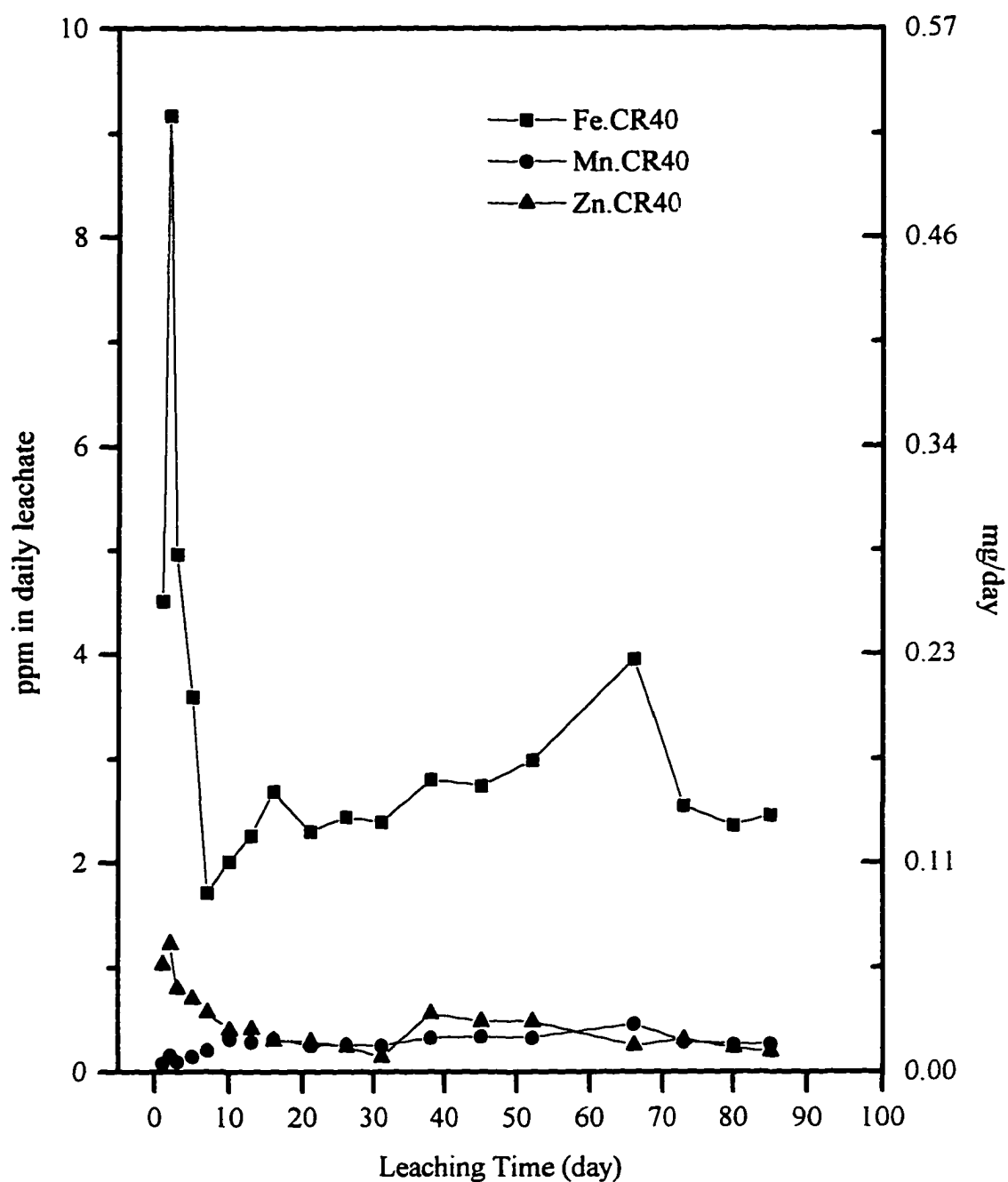


Figure 4.33 Leaching profiles of Fe, Mn, Zn from composted sludge mixed with Brooklyn soil using pH 4.0 solution

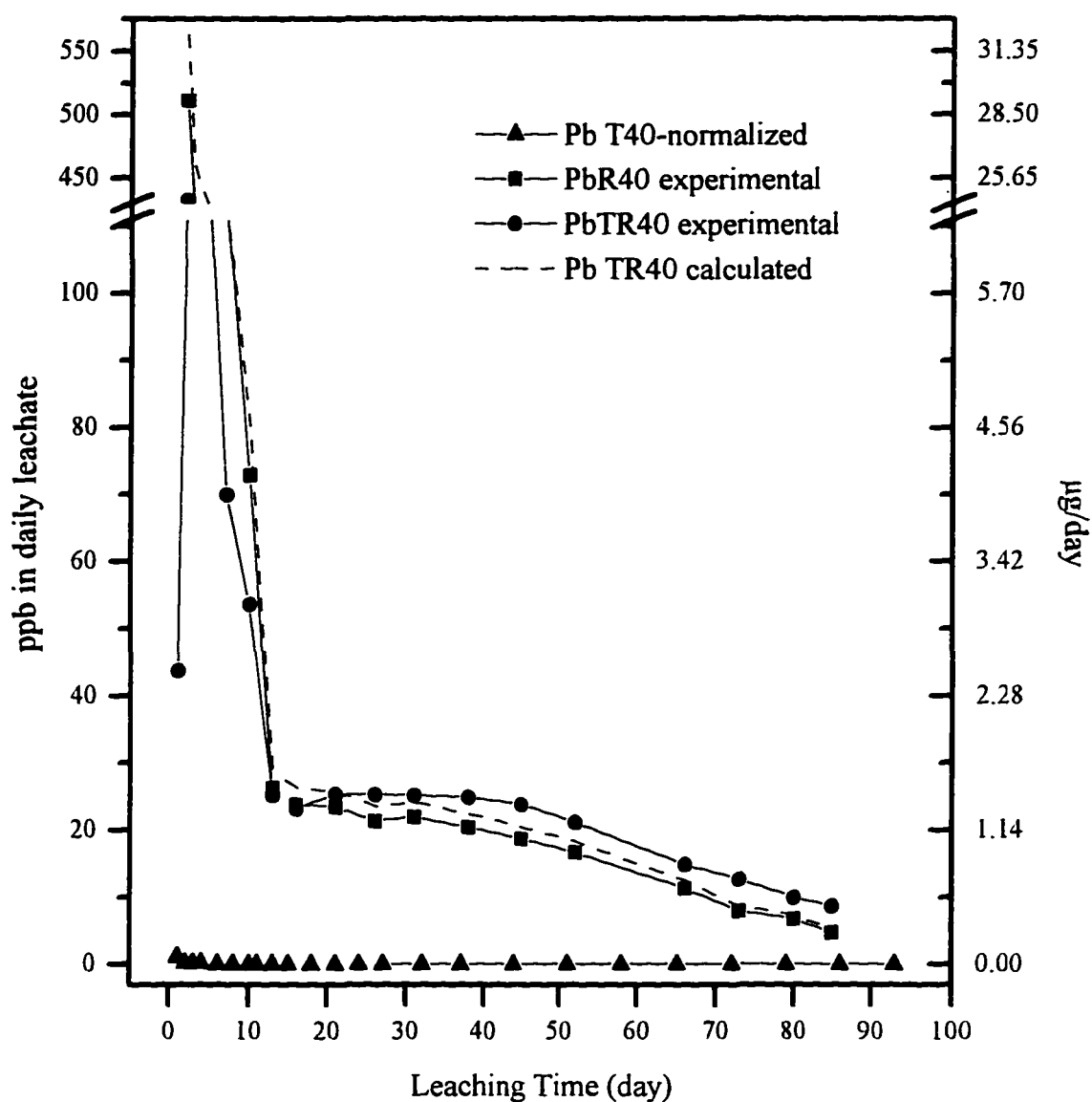


Figure 4.34 Leaching profiles of Pb from neat Brooklyn soil (R40), thermally dried sludge mixed with Brooklyn soil (TR40), and calculated Pb leaching profiles.

—■— Pb T40-normalized is the neat T40 profile normalized to the sludge usage in the mixture. It is here equal to the neat T40 profile multiplied by the ratio of 1.19g/50g.
 - - TR40-calculated is the sum of neat soil leaching profiles —●— Pb R40 and —■— Pb T40-normalized.

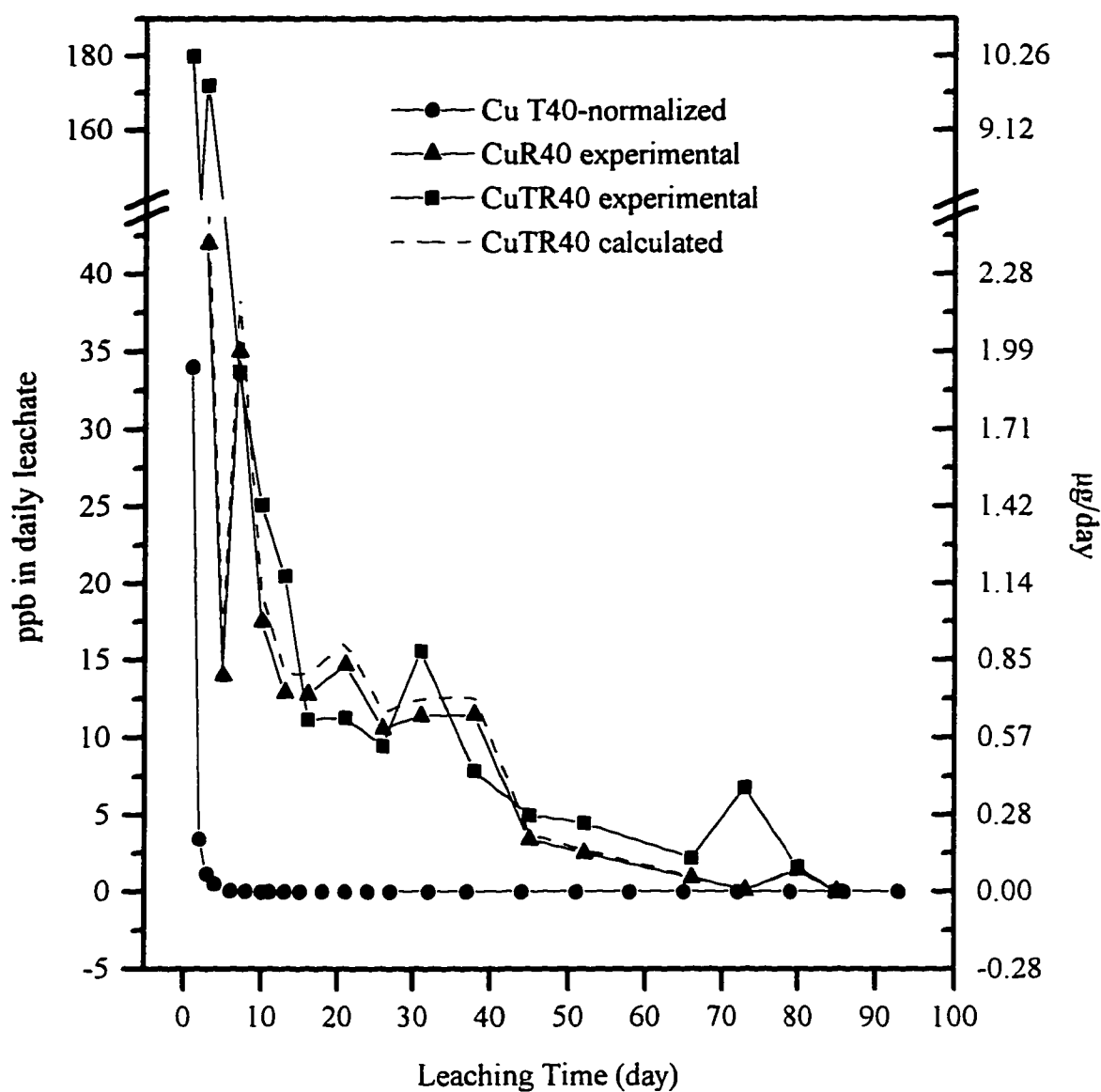


Figure 4.35 Leaching profiles of Cu from neat Brooklyn soil (R40), thermally dried sludge mixed with Brooklyn soil (TR40), and calculated Cu leaching profile.

—■— Cu T40-normalized is neat T40 profile normalized to the sludge usage in the mixture. It is here equal to the neat T40 profile multiplied by the ratio of 1.19g/50g.

- - TR40-calculated is the sum of neat soil leaching profiles —●— Cu R40 and —■— Cu T40 normalized.

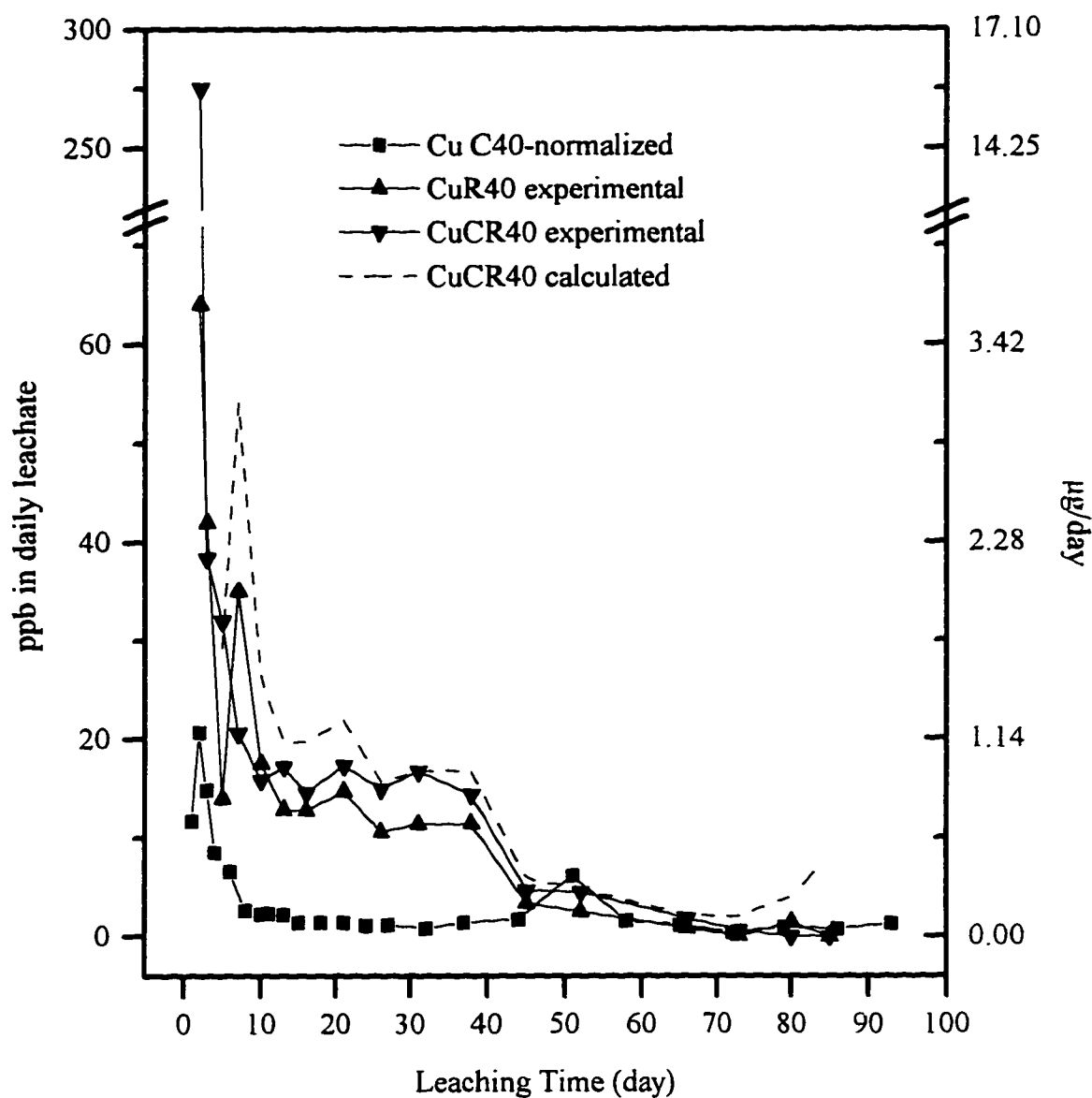


Figure 4.36 Leaching profiles of Cu from neat Brooklyn soil (R40), composted sludge mixed with Brooklyn soil (CR40), and calculated Pb leaching profiles.

—■— Cu C40-normalized is the neat C40 profile normalized to the sludge usage in the mixture. It is here equal to the neat C40 profile multiplied by the ratio of 2.02g/50g.

— — CS40-calculated is the sum of neat soil leaching profiles —▲— Cu S40 and —■— Cu C40 normalized.

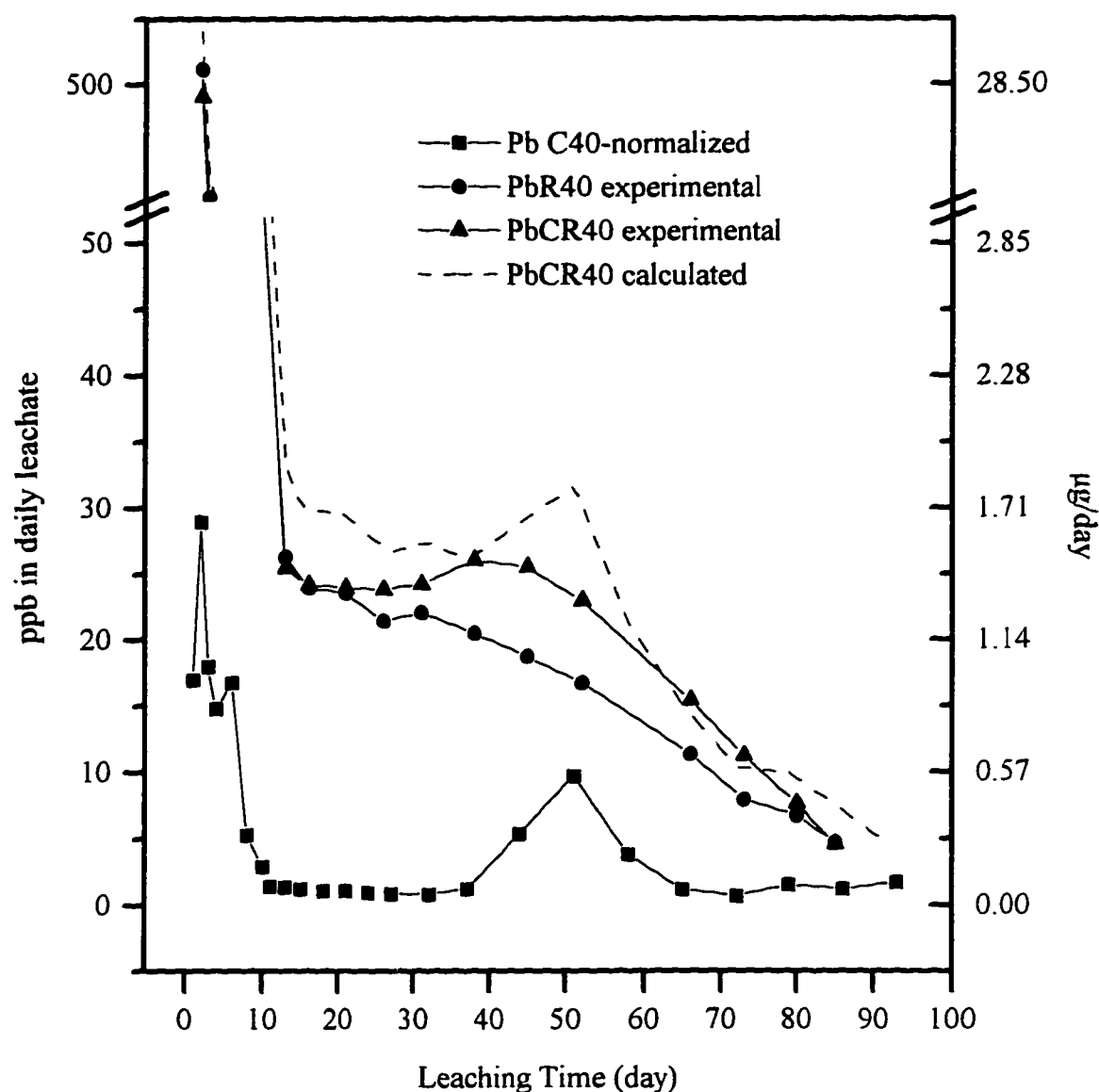


Figure 4.37 Leaching profiles of Pb from neat Brooklyn soil (R40), composted sludge mixed with Brooklyn soil (CR40), and calculated Pb leaching profiles.
 —■— Pb C40-normalized is the neat C40 profile normalized to sludge usage in the mixture. It is here equal to the neat C40 profile multiplied by the ratio of 2.02g/50g.
 —▲— CR40-calculated is the sum of neat soil leaching profiles —●— Pb R40 and —■— Pb C40 normalized.

little to the leaching profiles of the mixtures (Figures 4.28 and 4.29). Again, these all indicate that the thermally dried product, as a long range plan preferred by NYC, has a better leaching quality than composted sludge.

When high concentrations of heavy metals are leached from composted sludge, the Brooklyn soil shows strong retention of these metals. The dashed lines in Figure 4.36 and Figure 4.37 are simple superposition of the leaching profiles from neat Brooklyn soil and neat composted sludge with loads in the sludge-soil column. The CR40 leaching profiles from composted sludge mixed with Brooklyn soil column are under the dashed lines, but much close to those from the neat Brooklyn soil. The characteristic peak in leaching profile from the neat compost sludge (as seen in Figure 4.36 and Figure 4.37) is completely adsorbed by the Brooklyn soil. This implies that the Brooklyn soil, with more adsorption sites on organic moieties, acts as a sponge for metal ions, and could accept higher application rate of sludges with high contents of heavy metals compared to LI soil.

4.8 Conclusions

1. The lime requirement calculated using SMP method provides a large pH buffer capacity for sandy soil and urban soil during simulated rainwater leaching (pH from 4.0 to 4.5).

2. pH 1.5 leaching solution can completely leach almost all heavy metals in a 2 to 3 day period. However, no significant difference in leaching profiles from leaching solutions with pH value in the 4.0 to 5.6 range was observed. Inversely to the behavior of all other heavy metals, the leachabilities of molybdenum and selenium with the pH 1.5 leaching solution is extremely low because the elements occurs as oxyanions.

3. Leachates pH from three neat sewage sludge products using the pH 4.0 leaching solution remained at 6.0 for over 3 month continuing leaching period. This indicates the sewage sludge products from NYC have themselves a qualified pH buffer capacity for agricultural application without further lime treatment.

4. Heavy metals in the thermally dried sludge product show the least mobility, possibly because the thermal drying process destroys organic complexing agents and transforms the metals into oxide, carbonate, or sulfide forms. The metal complexes in dewatered and compost sludges are more leachable than in thermally dried sludge product.

5. Small amounts of metals were leached from dewatered sludge for 60 days continuing leaching because the leaching solution did not penetrate the dewatered sludge. This indicates that it is also difficult for

the nutrient contents to be leached for agricultural application in this period. However, when the dewatered sludge was completely wetted by the leaching solution, a large amount of heavy metals was leached, which could precludes agricultural application.

6. LI sandy soil originally contains less heavy metals than urban organic-rich soil from Brooklyn. After the small amount of heavy metal in soluble forms was quickly leached from the LI soil surface, the remainder may be held in the crystal structure of silicates and other resistant minerals and are therefore difficultly leached.

7. LI soil shows little retention of heavy metals from the two sewage sludge products, while the urban soil has strong retention of heavy metals leached from sludges. The concentration of heavy metals in daily leachates from all sludge treated soil columns through pH 4.0 to 5.6 solution were below the maximum contaminant level promulgated under the safe drinking water act regulated by 40 Code of Federal Regulations Part 257.

8. The annual whole sludge application rate for thermally dried sludge product is determined by copper content in the sludge, and 90 metric tons per hectare can be applied. However, for composted sludge, only 38 metric tons of compost sludge per hectare annually can be used for land application.

References

- 1 New York City Department of Environmental Protection, NYC
Sludge News, Spring 1992
- 2 F. Rockwell, Biocycle, 1993, 10, 55
- 3 R. M. Harrison, "Pollution Causes, Effects & Control", Royal
Society of Chemistry, London, 1990
- 4 United States Environmental Protection Agency, "Process Design
Manual Land Application of Sewage Sledge and Domestic
Septage", September, 1995
- 5 J. Roswell, Clear Waters, Summer 1988, 12
- 6 P. J. Matthews, CRC Crit. Rev. Environ. Control, 1993, 14, 199
- 7 S. E. Tisdell and V. T. Breslin, J. Environ. Qual. 1995, 24, 827
- 8 P. S. Yarlugadda, M. R. Mastsumoto, J. E. VanBanschoten, and
A. Rathuria, J. Environ. Engin., 1995, 121, 276
- 9 M. B. McBride, J. Environ. Qual., 1995, 24, 5
- 10 A. M. Dietrich and J. N. Jensen, Water Environ. Res., 1995, 67,
391
- 11 T. T. Eighmy, S. E. Krzanowski, D. S. Domingo, D. Strampfli, J.
R. Martin and P. M. Erickson, Environ. Sci. Technol., 1995, 29,
629
- 12 W. Shively, P. Bishop, D. Gress and T. Brown, J. Wat. Pollut.
Contr. Fed, 1986, 58, 234
- 13 L. Campanella, T. Ferri and B. M. Peronio, Sci. of Total Environ.,
1989, 27, 223
- 14 R. C. Kistler, F. Widmer and P. H. Brunner, Environ. Sci.

- Technol., 1987, 21, 704
- 15 R. P. Gambrell, *J. Environ. Qual.*, 1994, 23, 883
 - 16 E. A. Jenne, "Trace Inorganics in Water", in *Amer. Chem. Soc. Ser.* 1968, 73, 337
 - 17 G. F. Lee, *Prog. Water Technol.*, 1975, 17, 137
 - 18 A. E. Giblin, G. W. Luther and I. Valiela, *Coast. Shelf. Sci.*, 1986, 23, 477
 - 19 Paul F. Bell, B. R. James and R. L. Chaney, *J. Environ. Qual.*, 1991, 20, 481
 - 20 M. Leget, L. Divet and P. Marchandise, *Water Res.*, 1987, 21, 541
 - 21 R. B. Heimann, D. Conrad, L. Z. Florence, M. Neuwirth, D. G. Ivey, R. J. Mikula and W. W. Lam, *J. Hazard. Mater.*, 1992, 31, 39
 - 22 C.-H. Lee, H.-C. Wang, C.-M. Lin, G. C. C. Yang, *J. Hazard. Mater.*, 1994, 38, 65
 - 23 J. E. van Benschoten, *Water Environ. Res.*, 1994, 66, 168
 - 24 A. D. Tomlin, R. Protz, R. R. Martin, D. C. McCabe and R. J. Lagaco, *Geoderma*, 1993, 57, 89
 - 25 W. F. Pickering, *CRC Crit. Rev. Anal. Chem.*, 1981, 12, 233
 - 26 T. T. Chao, *J. Geochem. Exploration*, 1994, 20, 101
 - 27 D. L. Lake, P. W. W. Kirk and J. N. Lester, *J. Environ. Qual.*, 1984, 13, 175
 - 28 M. Kristen and U. Forstner, in "Trace Element Speciation: Analytical Method and Problems" CRC Press Inc., Boca Raton,

Fla. 1984

- 29 P. M. V. Nirel and F. M. M. Morel, *Water Res.*, 1990, 24, 1056
- 30 A. Tessier and P. G. C. Campbell, *Water Res.*, 1991, 25, 115
- 31 A. Tessier, P. G. C. Campbell and M Bisson, *Anal. Chem.*, 1979, 51, 844
- 32 T. T. Eighmy, J. D. Eusden, K. Marsella, J. Hogen, D. Domingo, D. Stampfli and J. E. Krzanowski, "Environ. Aspects of Construction with Waste Materials", Elsevier Science, Amsterdam, 1994
- 33 D. G. Ivey, M. Neuwirth, S. Shumborski, D. Conrad, R. J. Mikula, W. W. Lam and R. B. Heimann, *J. Mater. Sci.*, 1990, 25, 5055
- 34 P. C. Fung and G. G. Sanipelli, *Geoch. Cosmochim. Acta*, 1982, 46, 503
- 35 M. E. Farmer and R. W. Linton, *Environ. Sci. Technol.*, 1984, 18, 319
- 36 J. Scott and J.-C. Petit, "Aquatic Surface Chemistry", Wiley Interscience, NY, 1990
- 37 S. A. Baumann, M. D. Strathman, S. L. Suib, *Anal. Chem.*, 1988, 60, 1046
- 38 H. W. Neshitt and I. J. Muir, *Nature*, 1988, 334, 336
- 39 D. W. Mogk, *Rev. Geophys.*, 1990, 28, 337
- 40 K. Y. Cheng and P. Bishop, *Hazard. Waste & Hazard. Mater.*, 1992, 9, 163
- 41 R. Rubio, J. Huguet and G. R. Rauret, *Water Res.*, 1994, 18, 423

- 42 D. A. Skoog, "Principles of Instrumental Analysis", 3rd ed.,
Saunders College Publishing, Philadelphia, PA, 1985
- 43 Perkin Elmer, Atomic Absorption Spectrometer 3030B Operation
Manual, 1992
- 44 A. Montaser and D. W. Golightly, "Inductively Coupled Plasmas
in Analytical Atomic Spectrometry", VCH Publishers, Inc., NY,
1987
- 45 J. D. Ingle and S. R. Crouch, "Spectrochemical Analysis",
Prentice-Hall Inc., Engelwood Cliffs, NJ, 1988
- 46 Perkin Elmer, HGA-40 Operation Manual, 1992
- 47 G. Garnrick and G Schlemmer, Amer. Lab., 1991, 2, 120
- 48 A. T. Zander, Amer. Lab., 1976, 8, 11
- 49 L. M. Voth-Beach and D. E. Shrader, Spectroscopy, 1990, 1, 49
- 50 R. W. Dabeka, Anal. Chem. 1992, 64, 2419
- 51 J. E. Cantle, "Atomic Absorption Spectrometry", Elsevier, NY,
1982
- 52 J. A. C. Broekaert, F. Leis and K. Laqua, Spectrochim. Acta,
1979, 34B,73
- 53 S. S. Berman, J. W. McLaren and S. N. Willie, Anal. Chem.,
1980, 52, 488
- 54 J. A. C. Broekaert, F. Leis and K. Laqua, Talanta, 1981, 28, 745
- 55 S. Caroli, A. Farina, A. Laurenz and O. J. Senofonte, Anal. At.
Spectros., 1988, 3, 245
- 56 V. A. Fassel, Science, 1978, 202, 186
- 57 V. A. Fassel and G. W. Dickinson, Anal. Chem. 1968, 40, 247

- 58 T. Fukaya, M. Takeya and Y. Sayma, *Anal. Sci.*, 1993, 9, 727
- 59 United States Environmental Protection Agency, Method 200.15
1994
- 60 S. Yamasaki and Y. Tamura, *Commun. Soil Sci. Plant Anal.*,
1990, 21, 2017
- 61 A. Framzblau, L. Rosenstock and D. L. Eaton, *Environ. Res.*,
1988, 46, 15
- 62 M. Petrangeli Papini, M. Majone, O. J. Senofonte and S. Caroli,
Microchem. J., 1994, 50, 191
- 63 M. Thompson in "Analytical Performance of Inductively Coupled
Plasma- Atomic Emission Spectrometry", VCH Publishers, Inc.,
NY 1987
- 64 G. L. Long and J. D. Winefordner, *Anal. Chem.* 1983, 55, 712A
- 65 G. L. Walden, J. N. Bower, S. Nikdel, D. I. Bolton and J. D.
Winefordner, *Spectrochim. Acta*, 1980, 35B, 535
- 66 J. Davies and R. D. Snook, *Anal. At. Spectros.* , 1987, 2, 27
- 67 J. W. Olesik, L. J. Smith and E. J. Williamsen, *Anal. Chem.*,
1989, 61, 2002
- 68 W. A. van Borm and J. A. C. Broekaert, *Anal. Chem.*, 1990, 62,
2527
- 69 G. Horlick and K. W. Yuen, *Appl. Spectros.*, 1978, 32, 38
- 70 V. A. Fassel and B. R. Bear, *Spectrochim. Acta*, 1986, 41B, 1089
- 71 G. A. Petrucci and J. C. Van Loon, *Spectrochim. Acta* 1990,
45B, 959
- 72 I. B. Brenner and R. Binstock, *ICP. Inf. Newsletter*, 1993, 18,

473

- 73 R. J. Thomas and C. Anderan, *At. Spectros.*, 1989, 10,71
- 74 D. W. Burns, *Appl. Spectros.*, 1983, 37, 120
- 75 S. A. Myers and D. H. Tracy, *Spectrochim. Acta*, 1983, 38B, 1227
- 76 J. H. Kalivas and B. R Kowalski, *Anal. Chem.*, 1981, 53, 2207
- 77 J. M. Forster and C. Trassy, *Spectrochim. Acta*, 1981, 36B, 289
- 78 G. Batley and D. Gardner, *Water Res.*, 1977, 11, 745
- 79 M. B. McBride, "Environmental Chemistry of Soil", Oxford University Press, NY, 1994
- 80 R. A. Dahlgren, C. T. Driscoll and D. C. McAvoy, *Soil Sci. Soc. Am. J.*, 1989, 53, 1043
- 81 W. van Lierop, "Soil pH and Lime Requirement Determination" in "Soil Testing and Plant Analysis", 3rd ed., Soil Sci. Soc. Am., Madison, Wis., 1990
- 82 R. M. Sterrit and J. N. Lester, *Sci. Total Environ.*, 1980, 6, 55
- 83 H. D. Chapman, "Cation-exchange capacity" in "Methods of Soil Analysis: Chemical and Microbiological Properties", Soil Sci. Soc. Am., Madison, Wis. 1965
- 84 New York City Department of Environmental Protection, Chapter 1, in "Generic Environmental Impact Statements III", 1995
- 85 J. Zyman and C. A. Sober, *J. Wat. Pollut. Contr. Fed.*, 60, 2105
- 86 R. A. Dahlgren, D. C. McAvoy and C. T. Driscoll, *Environ. Sci. Technol.*, 1990, 24, 531
- 87 O. Hutzinger, "Reactions and Process", in "The Handbook of

- Environmental Chemistry", Vol. 2. Part D, Springer-Verlag, Berlin, 1985
- 88 A. Anderson and K. O. Nillson, *Ambio*, 1974, 3, 198
- 89 M. M. Benjamin and J. O. Leckie, *J. Colloid Interface Sci.*, 1981, 79, 209
- 90 T. L. Theis and L. E. Padgett, *J. Wat. Pollut. Contr. Fed.*, 1983, 55, 1271
- 91 R. C. Weast, "Handbook of Chemistry and Physics", 56th ed., CRC., Cleveland, OH, 1975
- 92 F. F. Mosey, J. D. Swanwick and D. A. Hughes, *Water Pollut. Contr.*, 1971, 70, 688
- 93 R. C. Stover, L. E. Sommer and D. J. Silviera, *J. Wat. Pollut. Contr. Fed.*, 1976, 48, 2165
- 94 M. S. Gold and E. J. Genetelli, *Water Res.*, 1978, 12, 889
- 95 H. Hohl and W. Stamm, *J. Colloid Interface Sci.*, 1976, 55, 281
- 96 M. M. Benjamin and J. O. Lecki, "Contaminants and Sediments", Volume 2, Ann Arbor Sci. Publishers, Ann Arbor, Mich., 1980
- 97 L. Saltzman, *Environ. Sci. Tech.*, 1985, 19, 328
- 98 T. Liroy, *J. Air Pollut. Contr. Assoc.*, 1978, 28, 51
- 99 A. T. Hanson and Z. Samani, *J. Environ. Engin.*, 1993, 119, 366
- 100 S. Dudka and A. Chlopecka, *Water, Air and Soil Pollut.*, 1990, 51, 153
- 101 B. K. G. Teng "The Chemistry of Clay-Organic Reactions", Aam Hilger, London, 1974