Speciation of chromium from industrial wastes and incinerated sludges

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Abstract

In this study, the Cr(III) and Cr(VI) contents of seven international standards, wastes, incinerated wastes and ash samples were measured with a simply hyphenated system. The Cr(III) and Cr(VI) content was measured using an on-line method, which contained an acid-activated aluminium oxide filled microcolumn that was developed especially for the study and an inductively coupled plasma atomic emission spectrometer. The sample introduction and the steps in on-line measurement were controlled by an autosampling program. For lower chromate concentrations, a similar, but off-line separation method was applied with an aluminium-oxide filled solid-phase extraction column and a graphite furnace atomic absorption spectrometer. Acid-activated aluminium oxide adsorbs the Cr(VI) in the pH 2–7 range, but does not adsorb the Cr(III). The adsorbed Cr(VI) can be eluted with strong acid. The changes in chromium forms were studied in the waste burning process as well. In our incineration studies, we obtained the following results: A portion of the chromium(III) content of wastes can be oxidised to chromium(VI) by the incineration process. It increases the potential risk of air and soil contamination of chromium(VI).

Keywords: Environmental analysis; Chromium; Metals

1. Introduction

The speciation of chromium has significant importance in the case of environmental samples, because chromium(III) is an essential micronutrient for mammals, while chromium(VI) is poisonous. The acceptable limits for these two chromium oxidation forms in soils, wastes and waters are very different in almost every country (Table 1). The evaluation of the real risk of chromium contamination in toxic wastes and soils requires a better knowledge of the fate of different chromium compounds in the waste management process and standardised methods for the measurement of chromium ionic forms. The two

main processes in sewage sludge waste management in Hungary and in New Jersey (USA) are landfill and incineration. Incinerated sludges are used in landfill also. The effect and fate of Cr(III) and Cr(VI) in soils are different. Cr(III) adsorbs strongly to the soil surface, does not leach out into the ground water and does not significantly increase the chromium content of plants. Cr(VI) can leach out easily into the deeper soil layers, so it can cause ground and surface water contamination. Cr(VI) can reduce to Cr(III) only in the top layer of soil and the rate of reduction depends on the pH and humic acid content of the soil. In our experience, there is no significant Cr(III) oxidation in sandy and chernozem soils [1].

Recently, many analytical methods have been published for the speciation of chromium, but there is no single, generally applicable method for every

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Table 1
Permitted Cr(VI), Cr(III) or total Cr concentrations in water, groundwater and soil in some countries

Medium	Comment	Source of data	Cr(III)	Cr(VI)	Total Cr
Water	Fresh acute criteria	Environmental Quality criteria in the USA	1700 μg/l	16 μg/l	–
	Fresh chronic criteria	Water quality criteria (EPA, 1991)	210 μg/l	11 μg/l	–
	Marine acute criteria		10 300 μg/l	1100 μg/l	–
	Marine chronic criteria		–	50 μg/l	–
	Drinking water		100 μg/l	100 μg/l	–
	Freshwater aquatic life	Environmental Quality criteria in Canada	–	–	2 μg/l
	Marine aquatic life	Water quality criteria (CCME, 1994)	–	–	–
	Livestock water		–	–	1000 μg/l
	Irrigation water		–	–	100 μg/l
	Drinking water		–	–	50 μg/l
Ground water	Water reservation area	Berlin intervention values	–	20 μg/l	50 μg/l
	Old river valley		–	30 μg/l	100 μg/l
	Highlands		–	40 μg/l	200 μg/l
	Reference values	Netherlands proposed intervention values	–	–	50 μg/l
Soil	Interim assessment criteria	Canada	–	2.5 mg/kg	20 mg/kg
	Draft law agricultural	Germany	–	–	100 mg/kg
	Target values	Netherlands	–	–	100 mg/kg
	Reuse values	Berlin	–	2.5 mg/kg	75 mg/kg
	Multifunctional levels	Kloke	–	–	50 mg/kg
	Max. allowed values	Switzerland	–	–	75 mg/kg
	Gardens	Eikmann-Kloke	–	–	100 mg/kg
	Parks		–	–	150 mg/kg
	Agricultural		–	–	200 mg/kg
	Industrial		–	–	200 mg/kg
	Gardens	UK	–	25 mg/kg	600 mg/kg
	Parks		–	25 mg/kg	1000 mg/kg
	Soil	Hungary	–	–	100 mg/kg

sample type. The methods involved are of three basic types:

(1) Selective detection: The detection system can separate or yield different responses for the Cr(III) and Cr(VI) ions. Included in this class are the UV–Vis photometric methods [2–9], stripping voltammetry [10] and, in some special cases, graphite furnace atomic absorption spectrometry [11].

(2) Off-line methods: The two chromium ion forms are separated in the sample preparation. Alkaline solutions [12,13] or organic solvents [14–16] are used for selective extraction of Cr(VI) or Cr(III).

(3) On-line methods: A separation system is connected to a detection system that gives the same signal for both of the chromium ion forms but, on the basis of signal changes over time, the ion forms can be identified. For the separation, high-performance liquid chromatography (HPLC), ion chromatography (IC) or flow-injection (FIA) methods are used; for detection, flame atomic absorption (FAAS),

inductively coupled plasma atomic emission (ICP–AES) or mass spectrometry (ICP–MS) methods are generally used. In the HPLC and IC separations, ion-exchange columns [17,18] or reversed phase (RP) C_8 [19], RP-18 columns [20–29] are used after creating an ion-pair between Cr(VI) and ion-pair creating reagents (APDC, DEDTC, TBAA). In FIA separations, complex-creating resins or aluminium oxide [30–35] are used as a separation adsorbent.

In this study, a cardinal issue was the fate of chromium(III) in the incineration process. Is it oxidised to chromium(VI)? The answer is important because the handling of non-toxic or less toxic chromium(III) is much easier than that of the toxic chromium(VI) form.

At present, there is no commercially available international standard solid waste sample for the speciation of chromium. For this reason, the chromium(III) and chromium(VI) concentrations of seven international samples were measured, offering

Table 2
List of studied international standard waste samples

No.	Type of waste	Official number of control sample	Producer
1	Solid waste laboratory control sample	SRS012 AX012	Fisher Scientific
2	Solid waste laboratory control sample. Fly ash	SRS001-100 AZ001	Fisher Scientific
3	Solid waste laboratory control sample. Municipal	SRS019-50 AY019	Fisher Scientific
4	EPA quality control	WP976	US Environmental Protection Agency
5	BCR trace elements in sewage sludge amended soil	BCR No. 143	Commission of the European Communities, Community Bureau of Reference
6	BCR trace elements in sewage sludge	BCR No. 144	Commission of the European Communities, Community Bureau of Reference
7	BCR trace elements in sewage sludge	BCR No. 145	Commission of the European Communities, Community Bureau of Reference

an opportunity for an inter-laboratory comparison. The samples were selected on the basis of waste type, as summarised in Table 2. We measured the total concentration of chromium in every sample, and the chromium(III) and chromium(VI) content of a 0.01 M $CaCl_2$ extract from the samples.

2. Experimental

For the preparation of waste samples for the measurement of total chromium content, 1 g of dry sample was measured. A Labor MIM (Budapest, Hungary) OE-718/A electronic block digestor was used for the wet digestion. The digestion consisted of two stages: (1) Pre-digestion: A 1-g amount of sample was incubated with 10 ml of conc. HNO_3 at 60°C for 30 min. (2) Digestion: A 3-ml volume of conc. H_2O_2 was added and the mixture was incubated at 120°C for 1.5 h. The volume of digested liquid was increased to 50 ml using deionized water and then filtered using MN (Macherey–Nagel) 640W filter paper [36].

The chromium concentration of the samples was measured using a Labtam 8440M ICP–AES instrument (Australia). The chromium signal was measured with a polychromator at 267.716 nm. The flow-rate of the peristaltic pump (Gilson, Minipuls 2) was 3.5 ml/min. A stop flow GMK nebulizer (Labtam, Australia) was used. The RF generator was crystal-controlled, operating at 27.12 MHz. The sample gas pressure was 360 kPa; the sample gas flow-rate was 1.14 l/min; the coolant gas pressure was 140 kPa; the coolant gas flow-rate was 15.3 l/min; the auxiliary gas pressure was 100 kPa; the auxiliary gas flow-rate was 0.3 l/min; the flushing gas flow-rate was 0.12 l/min; the forward power was 1200 W and the reflected power was <5 W. BDH (Poole, UK) standard ($CrCl_3$, 1 mg/ml) was used to prepare the calibration solutions. All chemicals used were of the highest purity available.

For the speciation of chromium, only weak extraction methods can be used because chromium(VI) is sensitive to reduction in acidic media and chromium(III) is sensitive to oxidation in strongly alkaline solution. The application of an acidic extraction agent, a long extraction time and a warm extraction solution should be avoided. In our experi-

ment, 0.01 M $CaCl_2$ was used for extraction [37]. The soil-to-extraction solution ratio was 1:10, the extraction time was 2 h. Samples were filtrated and stored in a deep freezer until they were required for analysis.

Acid-activated aluminium oxide was used for the separation of chromium forms. The basis of our earlier published method [38] is the following: Only the chromium(VI) is adsorbed by alumina. The adsorbed chromate can be eluted with strong acid. Acid-activated aluminium oxide (Aldrich, Germany) was placed in a silicon tube, which was connected to the ICP instrument between the nebulizer and the peristaltic pump. The on-line measurement consists of four steps: (1) Washing with 0.1% $Al(NO_3)_3$ solution. (2) The flow of sample through the column; Cr(VI) is adsorbed on the alumina while Cr(III) is not. In this step, the Cr(III) concentration of the sample can be measured. (3) Washing of the column with distilled water. (4) Strong (3 M) hydrochloric acid is passed through the column to elute the adsorbed chromium(VI). The method was controlled by simply programming the Gilson 222 autosampler. This program can control all of the steps of the separation. There are five positions for racks in the plate of the autosampler. In this method, four racks and two bulks are positioned on the plate. The two bulks are placed in the first rack position. The first bulk contains 0.1% $Al(NO_3)_3$ solution and the other one contains 3 M HCl. There are two rows and seven sample positions in every rack. There are two standard samples in all rows, therefore, 40 samples are measurable with one filling. With this autosampler program, the sample volume and every parameter can be controlled. This autosampler works as a flow injection system but does not contain an injection loop. The air bubbles do not seriously interfere with the measurement. Their effect is detectable at all times in the background signal, but they do not disturb the calculation of chromium(III) and chromium(VI) concentrations. The standard deviation (σ) of the background signal was 0.6 digits of response. The detection limits of the chromium forms were calculated at 3σ. Using this method, 0.5–5 and 4 μg/l were the detection limits for chromium(VI) and chromium(III), respectively. The detection limit is better in the case of chromium(VI) and depends on the sample volume, because the

method preconcentrates this ion form. The results of an automated calibration are presented in Fig. 1.

Interference by different anions (sulphate and phosphate) and pH on chromate adsorption on acid-activated aluminium oxide has been studied and published earlier [38] (Table 3). In the pH 2–7 range, the dominant form of Cr(VI) is the $HCrO_4^-$ ion. The hydrogenphosphate anion interferes with the chromate adsorption capacity of acid-activated aluminium oxide. If the sample contains this anion in large amounts, large sample volumes should be avoided. By using small (less than 500 μl) samples, the microcolumn–ICP method remains free of interference from anions.

When the chromium concentration of the sample was under the detection limit of this method, an off-line separation method was applied. An empty solid-phase extraction column was filled with 0.2–0.8 g of acid-activated aluminium oxide. After washing with 0.1% $Al(NO_3)_3$ solution, 5 ml of sample was sucked through the column. The solution flowing through the column contains only chromium(III), because the chromium(VI) was adsorbed on the column. Each column was used just once because acid-activated aluminium oxide is not an expensive adsorbent and an off-line cleaning process in this concentration range would be difficult and expensive. The concentration of chromium(VI) was calculated as the difference between total chromium and the measured chromium(III) concentration. For chromium measurement, a Unicam 939 QZ graphite furnace atomic absorption spectrometer was used. The chromium content of the samples was measured at 357.9 nm, atomisation was at 2500°C, the sample volume was 10 μl, an extended lifetime cuvette was used and Zeeman background correction was applied. The detection limit was 0.01 μg/l for chromium(III) and total chromium.

To study chromium(III) oxidation in the incineration process, the municipal digested sludge US Environmental Protection Agency (EPA) standard sample (4th in Table 2) was burned in a laboratory furnace at different temperatures (between 200 and 1000°C). After burning, the mass loss and the 0.01 M $CaCl_2$-extractable chromium(III) and -chromium(VI) concentrations were measured. The three BCR samples studied (5th to 7th in Table 2) were burned at 300, 500 and 800°C in a laboratory furnace (Denkal
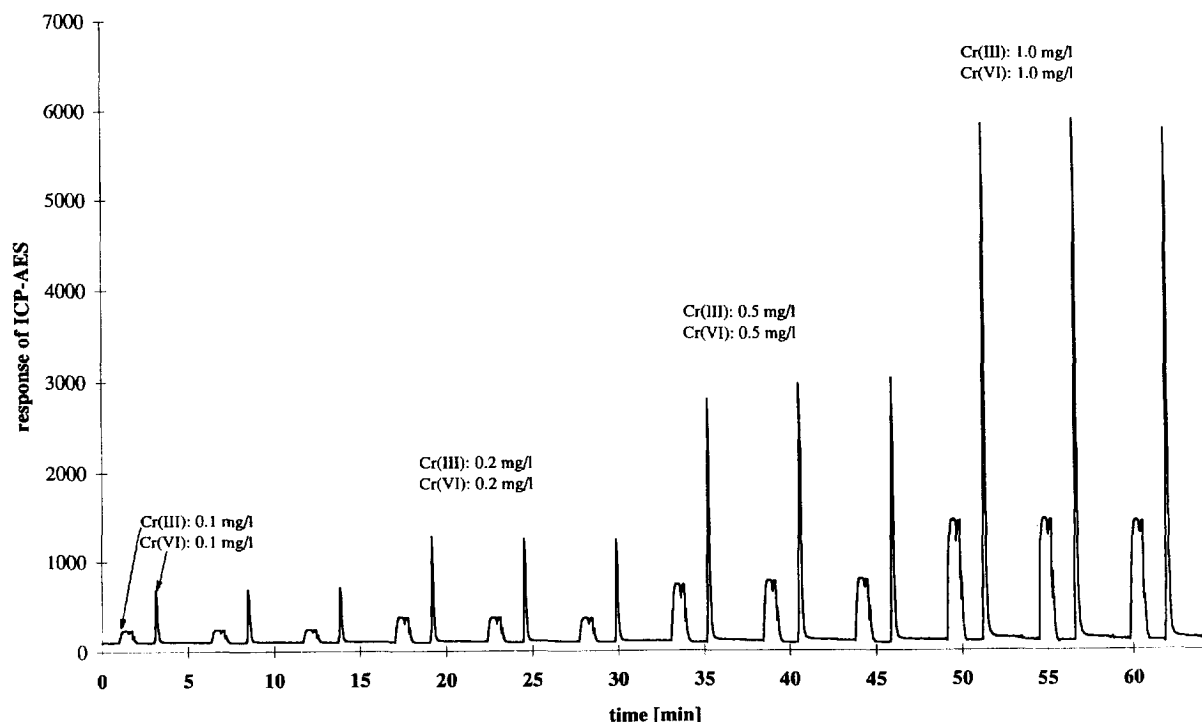
Fig. 1. Calibration with the automated on-line microcolumn–ICP–AES method. Every standard contained both chromium(III) and chromium(VI) at the same concentration. The reaction was performed in triplicate for each solution. The broad peaks are due to chromium(III) and the broadness of the peak is determined by the sample volume. The sharp peaks are the elution peaks of chromium(VI). The detection limit is 5 μg/l for chromium(III) and 0.5 μg/l for chromium(VI). In the chromium(III) peaks, there is a small amount of reproducible interference. This is caused by the air bubble at sample changing. This air bubble can cause a little, easily controlled interference only in this automated method.

4-K/1100, Kaloria GMK, Budapest, Hungary). After burning, the samples were extracted with 0.01 M $CaCl_2$, and the chromium(III) and chromium(VI) concentrations of the solution were measured.

3. Results and discussion

We have certified data on the total (aqua regia or hot HNO_3/H_2O_2-soluble) chromium concentration

Table 3
Effect of pH, sulfate and phosphate ratio on chromate adsorption capacity of acid-activated aluminium oxide

Interfering ion	Molar ratio of chromate and interfering anion	Chromate adsorption capacity of acid-activated aluminium oxide (mg/g) pH of solution:					
		2	3	4	5	6	7
None	–	1.92	3.49	4.13	4.00	3.93	2.16
Sulphate	1:1	2.09	3.54	4.36	3.79	3.81	3.04
Sulphate	1:10	0.26	1.29	1.19	1.32	1.03	0.97
Sulphate	1:100	0.11	0.40	0.27	0.33	0.31	0.28
Phosphate	1:1	0.32	0.35	0.37	0.44	0.36	0.23
Phosphate	1:10	0.22	0.25	0.27	0.33	0.22	0.10
Phosphate	1:100	0.13	0.13	0.11	0.08	0.07	0.04

Table 4
Comparison of the measured and certified chromium content of studied samples

Number	Certified chromium concentration values with confidence intervals (mg/kg)	Measured chromium concentrations (mg/kg)
1	164 600±13 638	164 000±1100
2	30.1±3.6	35.6±6.2
3	55.6±9.2	62.8±9.7
4	204.46±90	199±6.3
5	–	166±21
6	–	740±31
7	–	46.8±3.2

A description of the samples is presented in Table 2.
Every concentration is written with the 95% confidence interval of the chromium concentration.

of the first four samples (1–4 in Table 2). In these cases, there were no significant differences in the amounts we measured and the certified content of the samples. The total chromium concentrations are important parameters because they can be compared to the easily soluble fractions of chromium(III) and chromium(VI). In many cases, this comparison can help to identify the source of an unknown contamination and help to evaluate the real long- and short-term risk of waste application in the case of landfill. The measured and certified values are presented in Table 4.

The aim of the measurement of chromium(III) and chromium(VI) concentrations of the samples was to determine the dominant form of chromium in these sample types. The first three samples were the result of an incineration process and the last four were sludge samples that were not incinerated. The results of speciation measurements are presented in Table 5. The chromium(VI) concentration of the incinerated

samples was not significantly higher than that of the sludge samples. The chromium(VI)- and chromium(III) concentrations of sludge samples are determined by the source of the sludge and its treatment. If the sample contains organic matter and its pH is acidic or neutral, chromium(III) is the stable form of chromium, therefore, the chromium(VI) can reduce to chromium(III). In our study, the oxidation of chromium(III) in the incineration process is only suspected, not scientifically proven. In general, digested municipal sludge contains only chromium(III), as in our study. During incineration, the organic matter is burned, therefore, the concentration of metals in the ash is higher than at the outset. If there is oxidation, the chromium(VI) formed can cause more serious problems for the environment than the originally existing chromium(III).

The municipal digested sludge (sample no. 4) was burned at different temperatures and its 0.01 M

Table 5
Results of the measurement of 0.01 M $CaCl_2$-extractable chromium(III) and chromium(VI) concentrations of the studied samples

No.	Chromium(III) concentrations	Chromium(VI) concentrations
1	8700±43.2 mg/kg	410±23.6 mg/kg
2	24.8±3.2 µg/kg	213±5.3 µg/kg
3	36.5±1.2 µg/kg	150±9.4 µg/kg
4	1890±102 µg/kg	<0.1 µg/kg
5	12.8±2.1 µg/kg	2260±21 µg/kg
6	24.1±3.2 µg/kg	210±11 µg/kg
7	15.4±6.1 µg/kg	58±1.3 µg/kg

Description of the samples are presented in Table 1.
Every concentration is written with the 95% confidence interval of concentration.
The high concentrations (higher than 0.1 mg/kg) were measured with the on-line microcolumn–ICP–AES method and the others were measured with the off-line separation–GFAAS method as described in Section 2.

CaCl$_2$-soluble Cr(VI) content was measured. In Fig. 2, the results are presented for each burning temperature. A maximum chromium(VI) concentration was obtained at 500°C. These data are a proof of chromium(III) oxidation in the incineration process. We conclude that there is co-precipitation at higher temperatures. This sample contains more than 1.6% iron and other metals in relatively high concentration (518 mg/kg lead, 1095 mg/kg copper, 1323 mg/kg zinc); therefore, there is a chance that a solid-phase co-precipitation reaction of the chromate occurred. These results have two important consequences: (1) There is chromium oxidation in the incineration process and (2) the chromium(VI) formed is not water-soluble in every case. The other three sewage sludge samples (Nos. 5–7) were burned at 300, 500 and 800°C. Chromium(III) oxidation in these samples is also significant (Table 6). In the case of the

Table 6
Change in the 0.01-M CaCl$_2$-soluble chromate content of sewage sludge samples during the burning process.

Sample number	Cr(VI) content of incinerated waste samples (mg/kg)			
	Original sample	Temperature of burning		
		300°C	500°C	800°C
4	<0.0001	1.28	12.0	0.70
5	2.26	0.472	7.83	1.59
6	0.21	0.036	26.8	64.1
7	0.058	0.258	10.7	10.8

The waste samples (names and descriptions in Table 2) were burned at different temperatures.
These results show that there is chromium(III) oxidation in the incineration processes.
The amount of chromate formed is significant and can cause serious environmental problems in the case of landfilling of incinerated sludge samples.
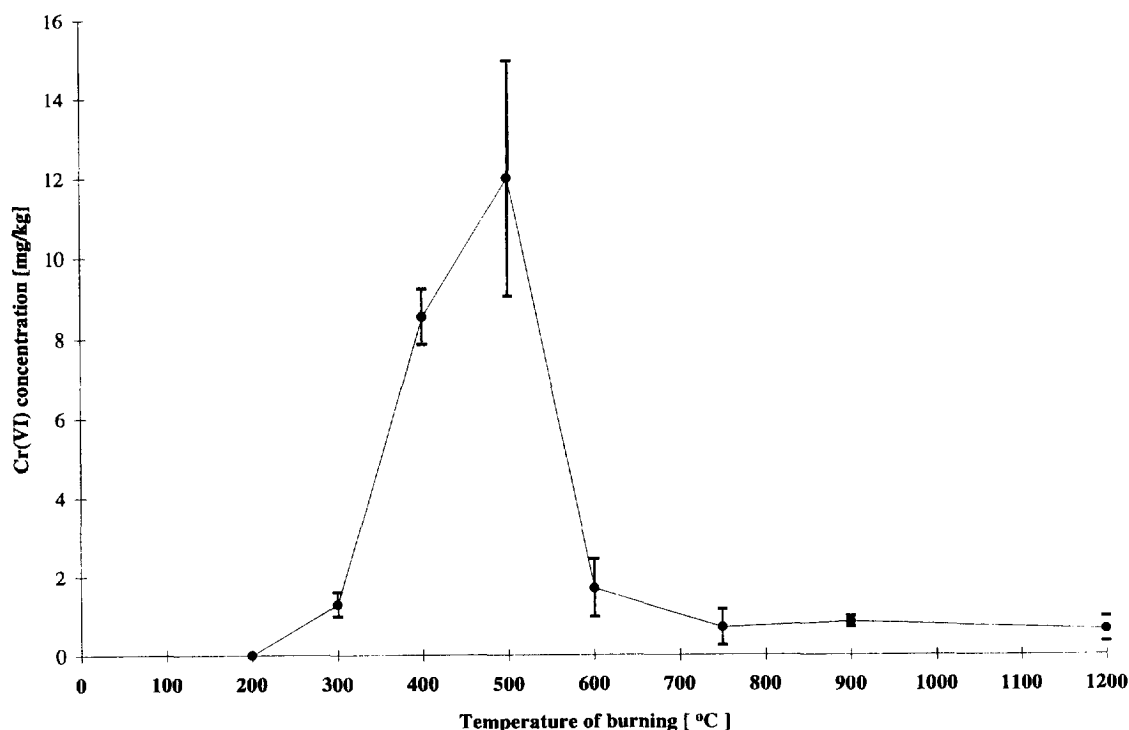

Fig. 2. Change in the 0.01-M CaCl$_2$-soluble chromate content of the municipal digested sewage sludge (No. 4) sample during the burning process. The sample was burned at different temperatures, in triplicate. The ranges indicate the confidence of values at the 95% level. There is a maximum chromate concentration at 500°C. We believe that there is co-precipitation of chromate at higher temperatures, therefore, the total chromate concentration of the sample would be much higher, but it is not a water-soluble chromate.

sewage sludge-amended soil sample (No. 5), the solubility decrease obtained was similar to that in the case of the municipal digested sludge sample (No. 4). This phenomena was not observed for other sewage sludge samples (Nos. 6 and 7); the soluble chromium(VI) concentration was the highest at 800°C.

Another interesting phenomena was observed in the comparison of the soluble chromium(VI) concentrations of sewage sludge samples (Nos. 5–7). In the cases of samples 5 and 6, the chromate concentration was significantly higher at room temperature than at 300°C (Table 6). This indicates that at lower temperatures, chromium(III) is the thermodynamically stable form of chromium, whereas at higher temperatures $(T>300°C)$, it is the chromium(VI) form. By first heating these samples, the thermodynamically unstable chromate changes to chromium(III); it oxidises the organic matter in the sample. At higher temperatures, the oxygen content of the air can oxidise the chromium(III) to chromium(VI). This indicates that 'cooking the samples' is healthy and the burning of waste is not.

4. Conclusions

This study has yielded two important results. We have an inexpensive and simple method for the on-line speciation of chromium and an off-line method for lower chromium(VI) concentrations. We obtained proof of chromium(III) oxidation in incineration processes, which can increase the ecological risk of high-temperature waste burning.

Acknowledgments

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