About Chromium (VI) Extraction from Fertilizers and Soils

Manfred Sager

Austrian Agency for Health and Food Safety Spargelfeldstrasse 191, A-1226 Vienna, Austria

Extractions from fertilizer and soil samples were performed to yield the operationally defined fractions of "soluble" chromate (extractable with NH_4NO_3), "exchangeable" chromate (extractable with phosphate buffer pH 7.2), and these results were compared with the data obtained by extractions with ammonium sulfate, borate buffer pH 7.2, saturated borax pH 9.6, and polyphosphate (Graham's salt). In order to maintain the pH of extractant solution about constant, the concentration of extractant buffer had to be raised to at least 0.5 M. The results strongly depended on the kind of extractant, and the solid: liquid ratio. For most of the samples investigated, the extraction efficiency increased in the order borate – sulfate – nitrate – phosphate. Whereas the recovery of K_2CrO_4 and $CaCrO_4$ added to the samples of basic slags prior to the extraction was about complete, the recovery of added $PbCrO_4$ was highly variable. In soil extracts, the color reaction was interfered from co-extracted humics, which react with the chromate in weak acid solution during the time period necessary for color reaction (1 hour). However, this problem can be overcome by standard addition and subtraction of the color of the extractant solution. In soil extract of about pH < 7, organic material reduced chromate during the extraction period also, and standard addition of soluble chromate is recommended to prove recovery and the stability of chromate in the samples. In admixtures of soils and basic slags, results for hexavalent chromium were lower than from the mere basic slags. This effect was more pronounced in phosphate than in nitrate extracts. As a proficiency test, samples low in organic carbon from contaminated sites in Hungary were tested. The results from NH_4NO_3 extracts satisfactorily matched the results of the Hungarian labs obtained from $CalCl_2$ extractants.

Key words : chromate, fertilizers, basic slags

1. INTRODUCTION

1.1. Sources of Cr(VI)

Hexavalent chromium compounds have been frequently used in electroplating, tanneries and leather production and in preservation of wood. CCA-solution (copper-chromate-arsenate) as it is used in New Zealand, Norway and elsewhere, consists of $CuSO_4 \cdot 5H_2O : Na_2Cr_2O_7 \cdot 2H_2O : H_3AsO_4$ =7 : 9 : 4, in 2-10% working solution (Carey et al. 2002). The yellow pigments $PbCrO_4$ and $BaCrO_4$ are not in use any more in Europe. Chromite ore processing residues may still contain about 30% of its chromium in the hexavalent state (James, 1994). Basic slag as a by-product of steel production has been used as fertilizer because of its 10 -16% phosphorus content. In this technical process, liquid pig-iron is oxidized by air, whereas phosphates and others are caught at the lime cover of the reaction vessel. Because hexavalent chromium is thermo-

dynamically stable under excess oxygen at these high temperatures, sometimes leachable hexavalent chromium may be formed.

1.2. Cr(VI) in soils and sediments

If soluble chromates are applied on soils, Cr(VI) is hardly retarded and moves rapidly down, unless it gets reduced to the trivalent state (Bartlett and Kimble, 1976; Zachara et al., 1989; Puls et al., 1994; Carez et al., 1996). On sediments, adsorption proceeded only partially. Some of this adsorbed chromium was found exchangeable in NH_4NO_3 or in $NH_4Cl/NaOH$ pH 7, the rest yielded the same leaching pattern like the original Cr(III) present in the sample (Sager, 1996). In aquifers, mobile chromate is stopped at pyrite, green clays, green rusts and other Fe(II)-bearing minerals, resulting in immobilization of Cr at clay minerals or ferrihydrite (Loyaux-Lawniczak et al., 2001).

Leachable hexavalent Cr has been known to be hazardous for a long time. This led to set a reg-

ulatory limit for chromate contents for waste deposits of 2 mg/kg, as well as chromate in effluents of 0.1 mg/L in Austria. Cr(VI) is stable in mineral nitrate and phosphate fertilizers as well as toxic to plant roots, and hazardous to ground water. In order to avoid abuse, the same limit of 2 mg/kg has been set for the use of mineral fertilizers used in agriculture.

2. MATERIAL AND METHODS

Fertilizer samples were crushed and homogenized in a rotating agate or a corundum mortar mill. Soil samples were air dried, and sieved minor 2 mm. The samples were weighed into glass Erlenmeyer flasks, 50 ml of various kinds of extractant solution was added, and shaken for 2 hours at ambient temperature. Occasionally, pH during extraction was determined with a glass electrode. After filtration, for spectrophotometric determination of hexavalent chromium, suitable aliquots of the extractant solution were pipetted into 50 ml volumetric flasks, some water was added to fill the vessel about ¾, then the samples were acidified with 5 ml 0.75 M H_2SO_4 (42 ml H_2SO_4 conc made up to 1 liter with H_2O) and immediately 1 ml of diphenylcarbazide reagent (0, 5% solution in 1:1 acetone/water) was added, mixed, and made up to the mark. After 1-2 hours, the absorbance of the resulting violet color was measured at 542 nm. Calibrations were done with 2/4/8/10 (microliters) in 50 ml; however, the curve would be linear up to 50/60 μg for a 1cm cuvette. Oven dried K_2CrO_4 (Merck pro analysi) was weighed for the primary 1000 mg/liter calibration solution, which was diluted to 20 mg/liter for working purposes.

The stability of Cr(VI) in the extractant solutions was frequently tested by adding K_2CrO_4-solution, solid $CaCrO_4$, and solid $PbCrO_4 \cdot PbSO_4$ pigment

("Siccomin-yellow L 1523", Reichhold Chemie AG, 1120 Wien, containing 9% Cr and 63% Pb) to the samples prior to wetting with the extractant solution. The recovery of hexavalent chromium in the color reaction was tested by addition of chromate solution prior to acidification.

$CaCrO_4$ was synthesized by heating stoichiometric amounts of dry $CaCl_2$ (2.22 g) and K_2CrO_4 (3.92 g) in a porcellain crucible, and subsequently leached with 9 ml hot water. The structure of the product was checked by X-ray diffraction.

3. RESULTS

3.1. Spectrophotometric determination
The final spectrophotometric determination of chromate with diphenyl carbazide in aqueous samples has been issued as an Austrian Standard Method (OENORM M) 6288 in 1991, and can be done easily (see also Oelschlaeger 1955, Froehlich 1959, Pilz 1966). During the color reaction time, improvement of the stability of the color was obtained by the use of acetone:water mixture 1:1 for the dye instead of ethanol. In the absorption spectrum, the maximum of extinction was very flat, and 542 nm, 544 nm, and 546 nm yielded equal sensitivity. In case of colored sample solutions (like alkaline soil extracts), the same amount of sample solution was acidified and diluted to 50 ml, but without dye, and taken as the sample blank. Chromate addition revealed, however, that Cr(VI) significantly reacted with the dissolved organics during the color reaction (see below). Interferences from inorganics were investigated in 1 M NH_4NO_3 and in 0.5 M phosphate buffer pH 7.2 (see Table 1), because these solutions yield the operationally defined fractions "soluble "chromate (German Standard DIN 19730), and "exchangeable" chromate (Kozuh et al., 1994, Milacic and Stupar,

Table 1. Interferences in the final spectrophotometric determination (μg in 50 ml).

	In 1M NH_4NO_3	In 0.5M phosphate buffer pH 7.2	In 0.5M phosphate buffer+0,5 M polyphosphate
	"soluble" Cr(VI)	"exchangeable" Cr(VI)	
Fe^{3+}	120	400	> 400
VO^{2+}	340	5	7
Mo	> 400	> 400	> 400
Mn	> 400	> 400	> 400
F⁻	> 2000	> 2000	> 2000
Br⁻	> 400	> 400	> 400

Table 2. Stability of the color in nitrate and sulfate solutions in closed vessels.

	Final [NO$_3$]	After 1 h	After 2 h	After 4h	After standing overnight
H$_2$O	0	100 %	98 %	91 %	54 %
	0.1 M	98 %	95 %	88 %	38 %
NH$_4$NO$_3$	0.4 M	85 %	78 %	65 %	14 %
	0.8 M	84 %	76 %	57 %	5 %
	0.1 M	100 %	99 %	92 %	45 %
(NH$_4$)$_2$SO$_4$	0.4 M	99 %	99 %	92 %	41 %
	0.8 M	102 %	101 %	94 %	43 %

Table 3. Effect of humics on the recovery of Cr(VI).

Color of soil extract at 542 nm	Cr(VI)- addition before the extraction	Cr(VI)- addition before the determination	Cr(VI) determination in the extract by standard addition
E=0.000	100%	100%	-
E=0.036	86%	81%	96%
E=0.079	68%	75%	105%
E=0.090	0	38%	-
E=0.217	0	-	No slope

1995), respectively. Some of the P-fertilizer samples can strongly buffer themselves, thus the P-buffer concentration had to be increased from originally 0.1 M to 0.5 M, to maintain the pH within reasonable limits.

Iodide is strongly interfering as well, but it cannot occur simultaneously with hexavalent chromium because of immediate redox reaction. High amounts of trivalent Fe could be masked in polyphosphate solution (Graham's salt). Usually, the solubility of Fe and V at circumneutral pH is much lower than the limits found here. If the nitrate is the main component of the fertilizer investigated, nitric acid can be formed in the acidification step, which may fade away the dye (see Table 2). Fading in ammonium nitrate is not due to the oxidation of ammonium ions, as can be shown from stable colours in equivalent ammonium sulfate solutions. However, determinations are still possible, if the nitrate matrix is matched in the calibration curve. Staying overnight resulted in substantial color fadings.

3.2. Effect of organics

For soils yielding appreciably colored soil extracts in phosphate buffer, addition of chromate before the extraction and immediately before the addition of the reagent showed that incomplete recovery derived mainly from the color reaction period (Table 3). The spike added at the start of the extraction could be recovered by standard addition to the coloured extract prior to the reagent, within certain limits.

In order to demonstrate the effect of co-extracted humics on Cr(VI) determination, a chernozem soil was extracted with 0.4 M NaOH to yield a brown organic rich solution. For this soil, adsorption of hexavalent chromium from phosphate buffer was just 5%, and from 0.4 M NaOH just 11%.

When a substrate for growing bacteria (Agro-Biosol) was extracted with 1 M NH$_4$NO$_3$, the recovery of 200 µg Cr(VI) added to 5 g sample was about zero. After membrane filtration of the extract through 0.450 µm, the slope of chromate determination in the extract was 92%, 61%, and 63% (3 replicates), but useless, as chromate was not stable in this sample.

3.3. Addition of solid chromates

The extraction of minor amounts of K$_2$CrO$_4$ and CaCrO$_4$ was not limited by their solubility. On or within clay minerals, adsorbed chromate anion is exchangeable. The recovery of chromate from PbSO$_4$ · PbCrO$_4$ (pigment "Siccomin Yellow") added to the fertilizer samples was significantly lower for phosphate fertilizers, but variable, and seemed to have a maximum at pH 7.5-8.

3.4. Effect of solid : liquid ratio during extraction

In order to test matrix and dilution effects, the solid : liquid ratio was varied widely (see Table 4), which significantly influenced the results, if aliquots were taken to reach the optimum determi-

nation range. The validity of the calibrations was checked by standard additions.

3.5. Effect of extractant pH

Slag and ash samples may contain appreciable amounts of alkaline compounds (see table 5). In case of significantly high extractant pH, recoveries are lowered because of hydroxide precipitation. The extracts were controlled for total chromium with flame atomic absorption (AAS). In order to maintain a more constant pH during extraction, therefore the concentration of the phosphate buffer extractant had been finally increased from 0.1 M to 0.5 M.

3.6. Choice of various extractants

The extractant anion may effect the extraction efficiency by precipitation and ion exchange effects.

Extraction with borates was the lowest (see Table 6). From 0.1 M and 0.5 M phosphate buffer solutions, Ca-phosphates like $CaHPO_4$ or $Ca_5(PO_4)_3OH$ should precipitate, but basic slags are usually low in Ca.

Table 5. pH shift due to sample dissolution and its effect upon the analytical result (1 g basic slag+50 ml 0.1 M phosphate buffer).

pH before extraction	pH after extraction	Cr(VI) mg/kg	Total Cr mg/kg
6.3	8.0	221	232
6.5	8.1	199	222
6.8	8.7	232	250
7.5	10.1	178	200
8.6	10.9	140	150
10.8	11.2	127	131

Table 4. Effect of solid: liquid ratio upon Cr(VI) concentrations (mg/kg) found in basic slags.

Sample	1 M NH₄NO₃			0.5 M phosphate pH 7.2		
	DK 10228	DK 8314	DK 7443	DK 10228	DK 8314	DK 7443
0.5 g /50 ml	-	-	-	14.0	200	-
1.0 g /50 ml	-	180	-	12.5	190	3.6
2.0 g /50 ml	1.9	118	0.8	9.1	143	2.9
5.0 g /50 ml	0.7	73	0.5	3.5	108	1.0
20 g / 50 ml	0.5	-	0.1	-	-	-

The experimental results indicate that the basic slag samples were surely the worst case of incomplete dissolution and re/adsorption in 1M NH₄NO₃ and 0.5M phosphate buffer oH 7.2. However, in order to achieve compatible results between various laboratories, the solid:liquid ration of the extractions should be standardized.

Table 6. Effect of various extraction solutions upon the Cr(VI) concentrations (mg/kg) found in basic slag.

2 g/50 ml	1 M ammonium nitrate	1 M ammonium sulfate	0.5 M phosphate buffer pH 7.2	0.5 M phosphate/ polyphosphate	0.5 M borate pH 7.2	Saturated borax pH 9.6
DK 8314	118	132	144	-	59	54
DK 7681	0.7	4	95	72	2.3	17.5
DK10228	2.6	3	11	21	-	-

Table 7. The effect of the interaction of soils with a basic slag on the recovery of Cr(VI).

Sample	Added soil	Soil properties			0.5M phosphate pH 7.2	1M NH₄NO₃	1M borate pH 7.2
		Soil pH	Humics	Carbonate	mg/kg	mg/kg	mg/kg
			% w/w	% w/w			
DK 8314							
	None				201	188	43
	+calcic chernozem	7.3	6%	15%	80	159	29
	+gleyic luvisol	6.6	2.5%	0	180	168	25
	+dystric cambisol	5.5	2.5%	0	40	139	23
DK 7681							
	None				92	10	7.2
	+calcic chernozem	7.3	6%	15%	21	13	7.6
	+gleyic luvisol	6.6	2.5%	0	57	19	13.4
	+dystric cambisol	5.5	2.5%	0	7	24	9.4

Table 8. Interlaboratory comparison of results for soil samples from a chromate - contaminated site in Nyiregyhaza/Hungary.

mg/kg	This study		Agric. University Debrecen			Nyiregyhaza Technical College Lab.		Environmental Lab. Debrecen	
	July 98		Oct. 97	March 98	Oct. 98	1997	March 98	Oct. 97	March 98
Extract →	1M NH$_4$NO$_3$		0.01M CaCl$_2$			0.01M CaCl$_2$		0.01M CaCl$_2$	
Sample I	18.2 ± 0.9	pH=4.5	-		24.0 ± 2.3	-	-	-	-
Sample II	< 0.1	pH=3.9	-		0.22 ± 0.02	-	-	-	-
Sample III	2.1 ± 0.1	pH=3.9	-		2.24 ± 0.15	-	-	-	-
Sample IV	10.9 ± 0,4	pH=6.4	13.2 ± 1.0	11.5 ± 0.9	11.4 ± 0.4	11.4 ± 0.1	7.8 ± 0.4	15.0 ± 0.5	12.7 ± 0.1
Sample V	8.9 ± 0.3	pH=6.6	11.4 ± 0.6	8.5 ± 0.5	8.4 ± 0.5	8.8 ± 0.1	5.3 ± 0.1	11.1 ± 0.8	9.3 ± 0.03

3.7. Recovery from mixtures of basic slags with soils

In a mixture of a basic slag and a soil (1 g+5 g), extracted chromate may react with other components from the soil or the basic slag, in particular with divalent Fe and humics. Table 7 shows the results obtained from extractions with phosphate and borate buffers of pH 7.2, as well as with unbuffered ammonium nitrate. If ion exchange is the main mechanism of Cr(VI) release, the affinity of phosphate to the solid is expected to be higher than of divalent chromate, tetraborate or monovalent nitrate, resulting in higher release into phosphate than into nitrate media. If the released Cr(VI), however, gets readily consumed by divalent Fe, nitrate may oxidize the divalent Fe more quickly than the chromate, and thus result in higher recovery.

3.8. Interlaboratory comparison

For determination of hexavalent chromium in soils, no certified reference material has been available yet, because of the lack of long-term stability. Thus, an interlaboratory exchange of samples was arranged by the Central Laboratory of Debrecen Agricultural University, Hungary, which provided some alkaline and low organic carbon soils sampled at a contaminated site in Nyiregyhaza (Table 8). No additional information about the samples were given. In spite of the large scatter of results from the basic slags presented in this study, the results obtained for soil samples from different laboratories were satisfactory.

The time scale of analysis indicates a gradual decline of the obtained concentrations of hexavalent chromium in the solid samples IV and V.

4. CONCLUSIONS

Basic slags may contain appreciable amounts of hexavalent chromium. The recovery from circumneutral soutions for subsequent spectrophotometric determination with diphenylcarbazide may depend on the extractant pH, the anion of the extractant electrolyte and the solid: liquid ratio. In admixtures with soils, degradation of chromate may take place during the extraction step also. In order to achieve comparable results, there is a need to standardize the procedure.

Results for samples from a chromate contaminated site, however, agreed satisfactorily within different labs, because soil organics and soil Fe may have already completely reacted during the contamination period.

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