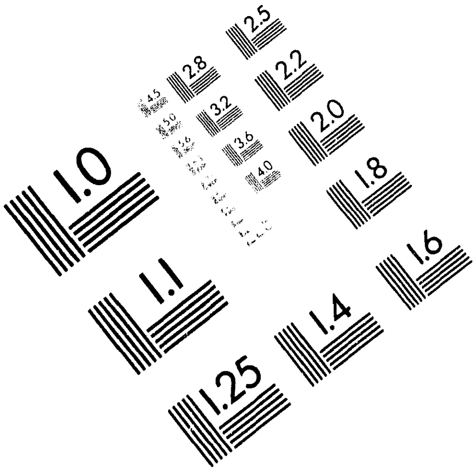

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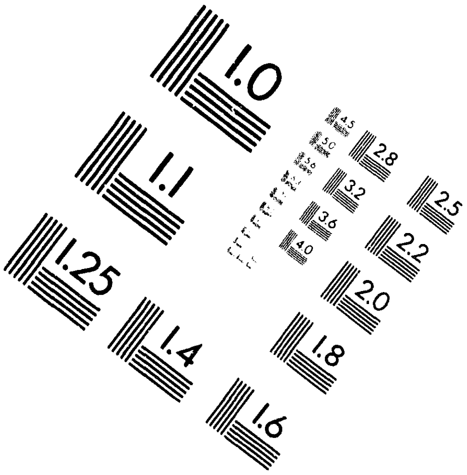

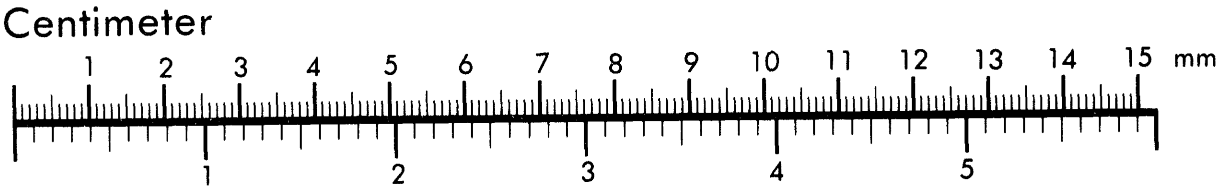

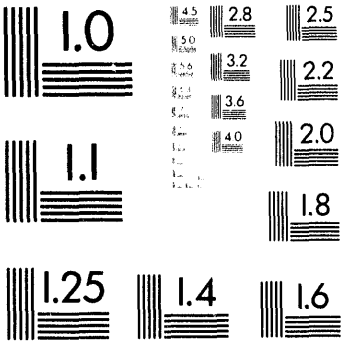

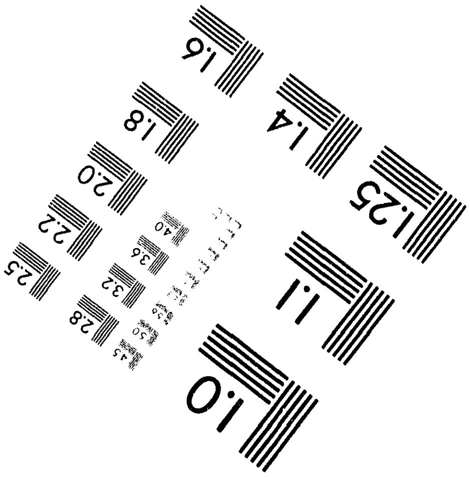

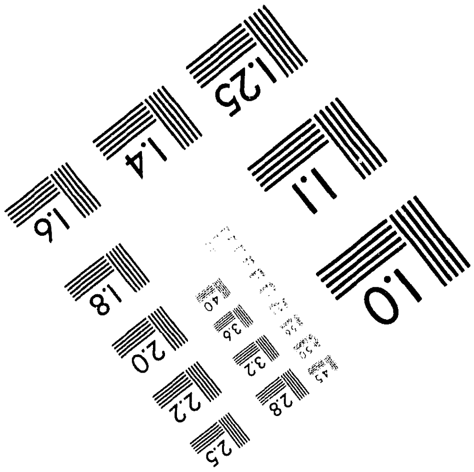

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Field Screening for Hexavalent Chromium in Soil-A Fast-Turnaround Field Method Based on Water Extraction

R. G. McCain
M. A. Baechler

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Field Screening for Hexavalent Chromium in Soil - A Fast-Turnaround Field Method Based on Water Extraction

R. G. McCain and M. A. Baechler
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INTRODUCTION

Sodium dichromate has been identified as a contaminant of concern at several waste sites on the Hanford Site. Although chromium standards for soil are typically stated in terms of total chrome, much of the toxicity and carcinogenicity are attributed to the hexavalent state, which typically exists as a relatively mobile anion. Investigation and removal of crushed drums potentially containing residual sodium dichromate required a field test for hexavalent chromium to support characterization and remediation activities. Previous experience with a commercially available field test kit had been unsuccessful. This stimulated an effort to determine potential sources of error in the field test and led to a number of modifications that significantly improved the reliability of the test.

BACKGROUND

The Hanford Site is located in southeastern Washington State. As part of the World War II Manhattan Project, reactors along the Columbia River were operated to produce plutonium for the Trinity device, World War II atomic bombs, and to support our nation's defense efforts during the cold war. Sodium dichromate was added to reactor cooling water as a corrosion inhibitor. Sodium dichromate and, to a lesser extent, potassium dichromate were also used in fuel processing and decontamination operations. Due to past discharge practices (e.g. disposing of waste directly to the soil column), elevated chromate levels have been detected in the groundwater of the unconfined aquifer.

The Sodium Dichromate Barrel Disposal Landfill was used in 1945 for disposal of empty crushed sodium dichromate barrels. Although reliable records are not available, it was considered likely that the site contained crushed empty drums with approximately 1% residual sodium dichromate present. When an expedited response action was initiated, it became obvious that a reliable field test for soluble hexavalent chromium in soil was required. Such a test would provide data necessary to support onsite decisions related to sample collection and site remediation.

CHEMISTRY OF CHROMIUM IN SOIL

Chromium may exist in a number of oxidation states, but the most common are the hexavalent and trivalent states. These two valence states have sharply contrasting chemical properties. Hexavalent chromium exists as an anion, is more readily extracted from soil and sediment particles, and is considered the more toxic form. Chromate is in pH-dependent equilibrium with other forms of hexavalent chromium such as dichromate, with chromate the predominant form at $pH > 6$. Trivalent chromium, on the other hand is much less soluble and absorbs to particles more strongly. The solubility of trivalent chromium compounds decreases above $pH = 4$ and above $pH = 5.5$ complete precipitation occurs.

Hexavalent chromium is the more stable form in equilibrium with atmospheric oxygen; however, it is a strongly oxidizing species. In the presence of soil organic matter, hexavalent chromium is reduced to trivalent chromium. Thus, in many soils, the relatively insoluble and less mobile trivalent chromium will tend to predominate, generally occurring as insoluble hydroxides and oxides.

Cleanup standards for chromium in soil are typically stated in terms of total chromium concentration. This is inherently conservative, since much of the chromium present is likely to be in the trivalent state, which is insoluble and immobile under ordinary circumstances. Much of the toxicity and carcinogenicity of chromium is attributed to the hexavalent state. However, this approach can become a trap when total chrome levels exceed the cleanup standard. For example, the Washington State Model Toxics Control Act sets a cleanup level for total chrome at 100 ppm.

ANALYSIS FOR CHROMIUM

A number of laboratory analytical methods are available for analysis of total chromium in soil. These include atomic absorption (AA), inductively coupled plasma (ICP) emission spectroscopy, and x-ray fluorescence (XRF). AA and ICP are typically performed on an extract or acid digest, in which trivalent chromium may be mobilized with hexavalent chromium. Most metals analysis is accomplished by either ICP or AA after digestion in concentrated nitric acid. Two alternatives are the extraction procedure (EP) toxicity test[4] (method 1310) in which the soil sample is extracted using an acetic acid solution at $pH = 5$, and the toxicity characteristic leaching procedure (TCLP) (method 1311). Analysis of the extract for metals is typically performed by ICP.

XRF methods may be used in the field to analyze soil samples with minimal preparation, or may be applied in a laboratory to analyze samples that have been ground to a consistent particle size or otherwise prepared. However, XRF also responds to total chrome, without regard to valence state. In fact, XRF analysis may respond to chromium locked in the mineral matrix which is not available even to acid digestion. Field XRF methods are also subject to interference from iron, both from peak overlap effects and secondary excitation. Hence, field XRF analysis for total chrome in soil is not practical in the presence of significant amounts of iron.

The laboratory methods available for determination of hexavalent chromium are designed for characterization rather than screening of samples. These methods typically require a lengthy extraction, sophisticated instrumentation, or generate an appreciable amount of waste. Also, the recommended holding time is only 24 hours. This results in many data validation problems associated with missed holding times, particularly at Hanford, where the sample must first be checked for total radioactivity before it can be shipped.

During sampling and remediation, it is important that areas of contamination be identified quickly, so that sample collection or soil cleanup can proceed. Lengthy delays waiting for laboratory test results are not practical or cost effective when equipment is operating in the field. What is needed is a fast and reliable field test that can be used to determine hexavalent chromium content in a minimum time.

FIELD TEST FOR HEXAVALENT CHROMIUM

The commercially available field test kit for hexavalent chromium employs an alkaline extraction, followed by colorimetric analysis of the filtered extract. Presence of hexavalent chromium is determined using the 1,5-diphenylcarbohydrazide (DPC) reagent, which produces a red-violet color. The alkaline extractant was specially developed to improve extraction efficiency for insoluble chromate compounds[5], e.g., those of calcium, strontium, mercury, silver, barium, and lead). A brief discussion of the original and modified test methods is provided below.

Original method (manufacturer's recommended procedure):

1. A soil sample is measured with a scoop and placed in a plastic extraction bag. Either 1 or 20 g is selected, depending on the anticipated chromate level.
2. A pre-measured amount of extractant powder is added to 40 mL of deionized water and mixed in a graduated cylinder. The solution is added to the extraction bag.
3. The soil/extractant mixture is shaken for 15-s at 2-min intervals over a period of 15 min.
4. At the end of the 15-min extraction period, the extract is filtered using filter paper and a funnel.

5. Two aliquots of the filtrate are transferred to 25-mL graduated cylinders. The aliquot size varies from 0.1 to 10 mL, depending on anticipated chromate content. Deionized water is added to both cylinders to a total volume of 25 mL. The contents of one cylinder are poured into a color viewing tube and set aside as a blank.

6. A pre-measured amount of the DPC reagent powder is added to the sample cylinder. The cylinder is swirled to mix the contents.

7. Following a 10-min reaction period, the contents of the second cylinder are poured into a color viewing tube and the color density is compared to the blank using a hand-held color comparator and an external light source. A calibrated color wheel is used to compare color development in the treated solution against the untreated solution. Both a long viewing path (axial) and short viewing path (transverse) are available, with a table provided for correction of long path results.

Experience with this test kit in the field was not satisfactory. Chromate standard was typically added to negative tests to check for interference. In many cases, the red-violet color failed to develop after chromate solution was added to the sample, indicating a potential interference. This stimulated a careful evaluation of each step of the test in an attempt to improve reliability. The following observations were made:

- The extractant is highly alkaline. When added to a typical Hanford soil, the resulting extract had a pH in the 11 to 12 range. Color development in the DPC reaction depends on an acid pH. Even though the DPC powder contains an acid buffer, the pH frequently was not reduced adequately for the reaction to take place. This effect is magnified when the test is being run for low concentrations, involving greater soil and filtrate aliquot quantities.

- Hanford soils can contain relatively high amounts of iron, which may interfere with the DPC reaction. The extractant appeared to mobilize some of the iron compounds present in the soil. This effect is also magnified when the test is run for low levels.

- Mixing of the DPC powder in the graduated cylinder was difficult, due to the long and narrow shape of the container. Although the powder dissolved, stratification of the solution was sometimes observed.

- In the field, lighting conditions may be erratic. Difficulties in matching the color wheel to the sample color were encountered at low concentrations of hexavalent chromium. This can affect the accuracy and repeatability of the tests.

Consideration of these factors led to a number of significant modifications in the test method, as summarized below:

1. The soil (20 g) is weighed, to an accuracy of ±0 .1 g, using a portable electronic balance.

2. The soil is transferred to a 2-oz, wide-mouth, glass jar with 40 mL of deionized water and a Teflon-coated stir bar. The jar is placed on a magnetic stirring unit for 15 min. Since the primary contaminant of concern is sodium dichromate, which is highly soluble, the use of the extractant provided in the kit is considered unnecessary. Using water alone also reduces the extraction of iron compounds and produces an extract with a more neutral pH. A magnetic stirrer unit provides more consistent and thorough agitation of the soil/extractant mixture.

3. Following the 15-min extraction period, the extract is allowed to settle for a few minutes and then filtered using a disposable vacuum filter unit with a 0.45-μ membrane. This filtration step is faster and produces a clearer filtrate.

4. Two aliqouts of the filtrate are transferred to 25-mL graduated cylinders. Aliquot size varies from 1 to 10 mL, depending on anticipated chromate content. Deionized water is added to make 25 mL total volume. One cylinder is set aside as a blank, and the contents of the second are transferred to a disposable beaker or small paper cup.

5. The DPC reagent powder is added to the cup and mixed by stirring with a disposable plastic stirring stick. The pH of the solution is checked with pH paper. If necessary, a few drops of sulfuric or hydrochloric acid may be added to achieve a pH of 6 or less. Stirring in an open container provides more effective mixing of the DPC reagent. Checking/adjusting the pH assures proper conditions for color development.

6. Following a 10-min color development period, 10 mL of the solution is transferred by pipet to a color cell. Color density is measured with a colorimeter, calibrated at a wavelength of 540 nm. If the results are offscale, 5 mL is removed from the color cell and replaced with 5 mL of deionized water, giving a 2:1 dilution. Another reading is made with the colorimeter. This process is repeated until a reading is obtained within the range of the colorimeter. Once a reading is obtained, a second aliquot of the original filtrate is diluted directly to the proper range and remeasured to provide a more accurate result.

7. If no color development is observed, 0.1 mL of a 50-ppm hexavalent chromium standard is added to the viewing cell. After allowing an additional 10 min, the chromate content is again measured. In the absence of any interference, a reading of approximately 0.5 ppm should be obtained.

COMPARISON OF RESULTS

The modified test method described has been used at a number of sites, including the sodium dichromate expedited response action site, but no chromate concentrations > 1 to 2 ppm have been detected in the field. All laboratory samples have also been negative. This is not particularly surprising, since the site was the location of buried, empty, sodium dichromate drums. Also, sodium dichromate is highly water soluble. Even in the relatively arid environment at Hanford, any residual sodium dichromate in the soil column is likely to have been washed down to the groundwater in the nearly 50 years since the crushed drums were buried.

Standard samples were prepared by mixing a potassium dichromate standard solution with representative soil and drying in a microwave oven. When analyzed by the modified water leach method described, recoveries in the range of 75 to 80% were obtained. Figure 1 shows a comparison of results obtained from analysis of the water extract with the hand-held comparator, colorimeter, and spectrophotometer. As expected, the quality of the results improves with increasing levels of sophistication in the measuring device.

SUMMARY AND CONCLUSIONS

A field test for hexavalent chromium in soil has been developed by modification of a commercially available field test kit and used in support of an expedited response action on the Hanford Site. The test is based on analysis of a water extract by the DPC method. It is recognized that the extractant included with the field kit may provide better results when dealing with less soluble chromate compounds. However, the primary contaminant of concern at Hanford is typically sodium dichromate, which is highly soluble. Thus a water extraction appears to be justified. This method is capable of detecting chromate compounds at sub parts-per-million levels. The red-violet color developed with the DPC reaction is very distinctive and has a very high absorbance index. Qualitative visual evaluation of test results is possible in the low parts-per-million range, well below typical action levels.

Additional modifications, such as weighing the soil, using a magnetic stirrer, vacuum filtration of the extract, and pH control during the color development phase were implemented to improve the overall reliability of the test. It is recognized that these modifications increase the support level and complexity of the test, since electrical power is required to operate the magnetic stirrers and the vacuum pump. Also, the test is no longer self-contained in a single box and additional consumables such as wide-mouth jars, filter units, disposable cups, and stirring straws are required. However, the test is still simple enough to be conducted under field conditions by properly trained personnel. The primary advantage is that results are available within 1 hr.

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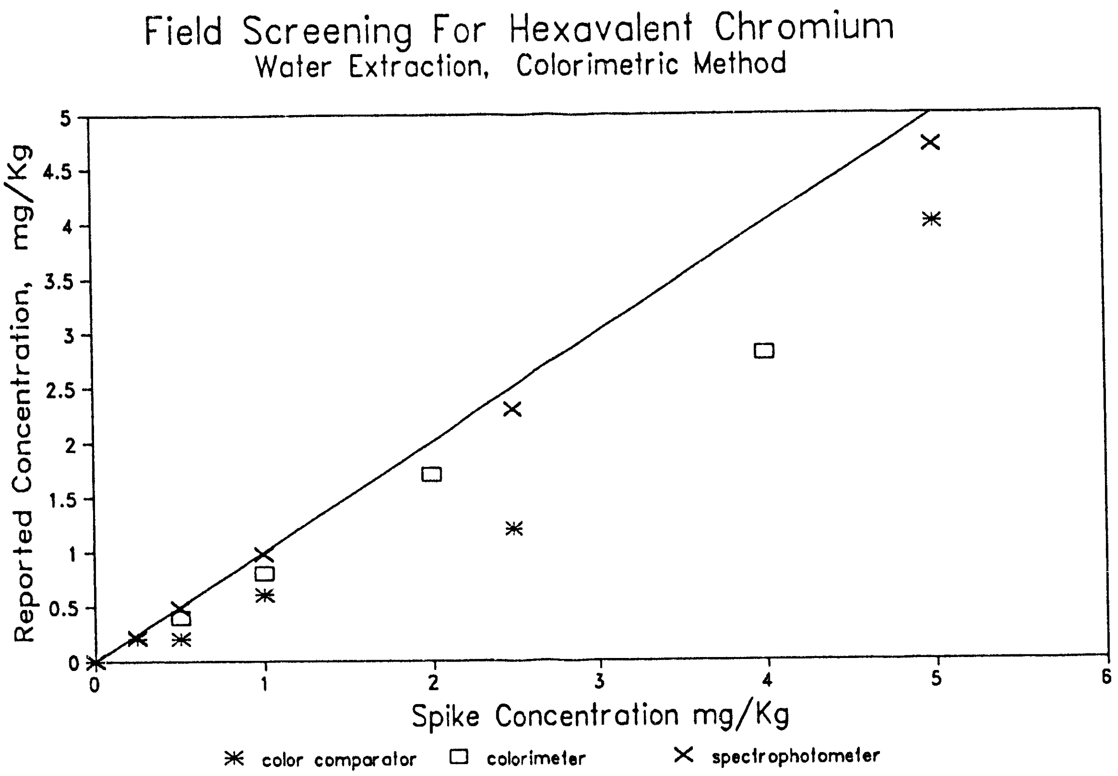
Field Screening For Hexavalent Chromium
Water Extraction, Colorimetric Method

FIGURE 1

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