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Panel Discussion: Analysis of Chromium: Methodologies and Detection Levels and Behavior of Chromium in Environmental Media*

by Michael Gochfeld†

In response to a variety of questions on alternative preparation and analytical methodologies, the Panel remarked on current analytical schemes and their detection levels. M. Gochfeld (UMDNJ-Robert Wood Johnson Medical School) noted that the difficulty of distinguishing Cr^{III} versus Cr^{VI} remains and that the same environmental soil sample may be reported by different laboratories as nearly all Cr^{VI} or nearly all Cr^{III}. The methods discussed included atomic absorption spectrophotometry (AA), inductively coupled plasma spectrophotometry (ICP), ICP followed by mass spectroscopy (ICP-MS), and X-ray fluorescence (XRF).

Questions were raised regarding new techniques such as photoelectron spectroscopy for detecting chromium (III) and (VI). S. Shupack (Villanova University) and S. Katz (Rutgers University) considered that X-ray diffraction can also distinguish the two forms, but that the limits of detection vary with specific methods and media.

Katz and Shupack emphasized that whether the final analysis is performed by XRF, chemiluminescence, AA, or ICP, one is measuring total chromium. It is the preparation of subsamples in different ways that allows one to determine the proportion of trivalent and hexavalent chromium.

R. Wedeen, who is in the process of developing *in vivo* XRF techniques for lead, raised the question of whether XRF could be used for chromium *in vivo*. Shupack responded that it is hard to know whether this method can be practical. *In vivo* techniques such as XRF and neutron activation analysis seem to be better for the detection of superficial distribution of elements and might not yield information on the burden in deeper organs such as the liver or kidney. But Wedeen pointed out that at least for XRF measurements of lead, the use of K rather than L radiation does allow deeper detection.

Shupack raised the question that since the half-life of chromium in the body is about 1 month, would it be possible to estimate the body burden by developing a provocative chelation technique similar to that used for lead. As a basis for studying this in animals, he noted that he has used acid digestion of organs to get tissue levels and that one would have to study the efficiency or yield of chelation in reference to these levels which can serve as a "gold standard" for calibration of the challenge technique.

The question of what happens to Cr^{III} in the higher pH system during the analytical extraction was posed Katz, who noted that there is a potential for oxidation at high pH particularly over time. He added, "I don't think I've had that problem. My Cr^{VI} usually ends up in the (VI) fraction and my Cr^{III} in the (III) fraction. That isn't to say that we couldn't see transformation over long time periods. Therefore when I spike a sample it is done freshly for each particular experiment. I think both the thermodynamic feasibility and the kinetics are important in understanding chromium transformation."

There was confusion over the recovery efficiency of spiked samples, particularly as they might reflect the microgram concentrations found in air samples. Katz noted that he had excellent recovery of a 1-mg spike in a 250-mL sample.

Katz noted that a radiotracer would very nicely tell you if there is a dynamic conversion. If you have a quantitative recovery of the spike, but less than quantitative recovery of the tracer, there is a conversion.

P. Lioy and others raised the question of the sensitivity or minimum detection limits of current analytic methods for detecting very low levels of chromium in

*Moderator: Michael Gochfeld. Panelists: Sidney Katz, Saul Shupack, Richmond Bartlett, and Carl Palmer. Participants: Paul Lioy, Richard Weeden, and Charlotte Witmer.

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environmental samples such as air samples. Lioy noted that AA seems to be adequate for samples of chromium in the 1 mg range, but asked what needs to be done to measure samples of the order of 100 to 300 μg such as would be found on air filters.

Shupack noted that ICP can be used satisfactorily at that range, but also called attention to a chemoluminescence technique which would detect levels down to 0.1 ppb. However, he reiterated that as we keep lowering our detection limits, we get to the point where we will be analyzing for everything we have ever had in our laboratories.

Lioy noted that environmental samples, particularly air, are going to be at very low concentrations to begin with, and sample preparation in the laboratory is simply going to have to be more careful than what is currently used for AA.

Shupack responded that graphite furnace atomic absorption can measure chromium in the part per billion range but that ICP is more convenient. Gochfeld asked whether ICP-MS, which is now becoming available, would be advantageous, and Shupack noted that it should do little better than currently available techniques, but reminded the audience that we were still talking about techniques for measuring total chromium only.

R. Bartlett (University of Vermont) noted that an old standby, the diphenyl carbazide test, is still a reliable way for getting the hexavalent component. You can oxidize chromium with manganese, then reduce the manganese with hydroxylamine to get the total chromium. The formation of the diphenyl carbazide complex is so rapid that even at very low levels of chromium organics do not interfere. He noted that it was possible to push this system to a detection level of 50 μg/kg (ppb), although usually the level is higher, and Katz suggested it was similar to flame atomization, which offers a detection level of around 500 ppb.

The audience posed several questions regarding the form in which chromium originally enters the environment, specifically in the case of the Oregon plating plant, but also generally as in incineration of sewage sludge or municipal solid waste. C. Witmer questioned the relationship between the black slag and the distribution of lead in the contaminated soil. C. Palmer (Oregon Graduate Center) noted that in Oregon the chromium was derived from the plating bath, an acid mixture of metal salts, the exact character of which remains undisclosed. However, it is likely that potassium dichromate was a major constituent. The lead is derived from the lead electrodes, which gradually dissolved in the bath. Palmer noted, in response to questions regarding the barium and calcium chromates that were measured, that both of these are available abundantly as free cations in the local soil.

The audience was impressed by the amounts of chromium present in the soil and raised the question of why people were not trying to reclaim it from the waste. Palmer noted that reclamation and recycling has been considered, but at present prices of chromium and costs of landfilling, it is more economical to landfill than recycle the waste.

Bartlett noted that the time to consider recycling was before the waste was discharged, and there was, of course, general consensus that this would certainly have been worthwhile. Bartlett noted that to really clean up a site, to lower the levels of contaminants to ambient levels, is really very costly and should still make recycling of recovered waste feasible in some cases. Palmer noted that in Oregon at least, the high cost was in retrieving the chromium waste from the soil and groundwater, and that this cost existed whether recycling or landfilling was chosen.

A question was posed regarding the adverse health effects on the people who tore down the building in Oregon. Palmer noted that all the work in the building was performed by an experienced hazardous waste remediation company whose employees took excellent precautions with regard to personal protection. Employees did not go into the building unless they were protected. They discovered an old boiler covered with asbestos. They remained fully protected until the asbestos and the chromium were removed both mechanically and by steam cleaning.

The audience voiced substantial interest in how well we understand the physical and chemical dynamics of chromium in soil, both in general, and particularly in relation to contaminated New Jersey sites. Gochfeld questioned whether given the complex nature of the interactions of chromium in environmental media, we still need more information on its behavior in the Hudson County soils. Shupack replied that he could not be confident at this time that there is adequate site-specific information. It was particularly remarked that in Hudson County, New Jersey, much of the chromium is not in soil, *per se*, but in slag and other modified materials. Bartlett responded that location is not important because chromium has physical and chemical properties that can be understood and regardless of the source, you can treat the sample as a special soil and study it as a soil. Bartlett argued that the same principles apply, that soil types differ from one another, and that slag is just a different soil.

Gochfeld inferred from Bartlett's comments that when you have a particular case, it is appropriate to actually do an extensive investigation on that particular material, rather than try to generalize, and Bartlett concurred that you have to go in and study what is there empirically. This led to the conclusion that site-specific study is unavoidable, although one can begin from generic principles.

By way of example, Gochfeld asked how heterogeneous are soils over space, for example, how many significantly different soils would one find in a square mile area, or an area the size of the Rutgers campuses, for example, or, more generally, what is the spatial scale of soil variability, and how many discrete empirical investigations would we have to mount.

The panel felt that this could not be answered in general terms. In some places soil is homogeneous over large areas, whereas in others it varies dramatically on a local scale. Bartlett summed it up by saying soils are different, and although you can use principles you have learned from all other soils to make predictions for the current investigation, it is impossible to generalize. If you are interested in a particular soil, you have to characterize it.

Incineration of sewage sludges and municipal solid wastes was identified as a major potential source of environmental chromium contamination, and the question was raised regarding existing analytical work done on the transformation of chromium to the hexavalent state during different stages of the incineration process. The panel noted that in incineration or even in a trash-to-steam facility there is a significant transformation with oxidation of Cr^{III} to Cr^{VI}. Whether it remains in that form when the ash is collected and transported has not been measured. The current measure is the EP toxicity test,* which identifies its toxic potential, but Bartlett cautioned that the standard EP toxicity testing is a sure way to miss hexavalent chromium since it is reduced in the test system.

Gochfeld noted that there is a lot of concern about incineration since some risk assessments identified hexavalent chromium as a major contributor to the total potential risk from incineration. That hinges on assumptions regarding the proportion of total chromium that is emitted from the stack and the proportion which is hexavalent. The data obtained from operating facilities are too sparse at this time to answer that question. Hence, risk assessors may use estimates as low as 1 % hexavalent and as high as 100%. The panel agreed this is clearly a research need. It is also important to understand what happens when oxidized chromium gets into a pollution control device or what atmospheric properties might influence its conversion when it is finally emitted.

*The EP toxicity test refers to a specific extraction procedure mandated for use to determine whether waste is hazardous. This ruling falls under the Resource Conservation and Recovery Act of 1980, which designates that any waste material containing toxic material at levels greater than those specified in the regulation is considered hazardous waste.