Determination of the Priority Pollutant Metals – Regulations and Methodology

Application Note

Atomic Absorption

Author

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Introduction

With the realization that industrial man introduces potentially hazardous substances into the environment, there has been increasing concern over the potentially detrimental effects of man-generated pollution. Metals are a unique environmental and industrial pollutant in that they are found naturally distributed in all phases of the environment. They are not created by man, but through industrial processes they are transported, concentrated, and transformed into various products. Often this results in human exposure to much higher concentrations or different chemical forms than those naturally present in the environment.

Various federal and state agencies, and private sector industrial and academic research participants have co-operated in studies describing the source, magnitude, distribution, and environmental and toxicological impact of trace metal pollutants, as well as consideration of natural sources of trace metal concentrations. These agencies, one being the US Environmental Protection Agency (EPA), have been legislatively assigned the difficult task of designating maximum allowable concentration levels as well as the regulation of industrial pollution at those levels.

Drinking Water Regulations

A main area of concern was the safety of public drinking water. Under the directives of the Safe Drinking Water Act of 1974, the EPA initiated the National Interim Primary Drinking Water Regulations (NIPDWR) in 1975. Primary Drinking Water Standards were established for the regulation of eight metals, as listed with maximum allowable concentrations in Table 1 [1].

Table 1. Maximum Allowable Levels in Drinking Water (mg/L)

USEPA Maximum allowable levels in drinking water (mg/L)	
Arsenic	0.05
Barium	1.0
Cadmium	0.01
Chromium	0.05
Lead	0.05
Mercury	0.002
Selenium	0.01
Silver	0.05

The Primary Drinking Water Regulations were established to protect public health, but secondary regulations were proposed to control such qualities as taste, color, and odor. The Secondary Drinking Water Standards include the regulation of four other metals, listed with maximum allowable concentrations in Table 2 [1].

Table 2. Secondary Maximum Contaminant Levels in Drinking Water (mg/L)

Secondary maximum contaminant levels in drinking water (mg/L)	
Copper	1.0
Iron	0.3
Manganese	0.05
Zinc	5.0

Though the Primary and Secondary Drinking Water Standards do not include regulation of sodium at this time, the EPA has recommended that states voluntarily establish programs for regular monitoring of sodium levels in public drinking water. Proposed amendments to the Safe Drinking Water Act establish guidelines for sodium concentrations. With this information, consumers who must restrict dietary consumption of sodium could if necessary make adjustments to their diets or seek alternate sources of drinking water when certain levels are exceeded. With evidences that excessive intake of sodium contributes to increased blood pressure and to hypertension in susceptible people, the EPA has recommended a maximum level of 20 mg/L for public drinking water [2].

Effluent Regulations

A second area of concern was control of water pollution through the regulation of industrial effluents. Legislative concerns over water pollution resulted in the passage of the original Federal Water Pollution Control Act (FWPCA) in 1948. This act and its numerous more recent amendments are often referred to as the Clean Water Act (CWA). Originally, regulatory responsibility for pollution control belonged to the Department of Health, Education and Welfare (HEW), but was transferred to the Department of the Interior in 1966. The EPA was formed in 1970, at which time it took on the responsibilities for water pollution control previously held by the Department of Interior. Since that time, with subsequent amendments to the FWPCA, additional federal programs have been created to meet water quality goals [1].

The Federal Water Pollution Control Act Amendments of 1972 established a comprehensive program to restore the quality of the nation’s waterways. Its goals were to make U.S. waterways fishable and swimmable by 1983 and to eliminate the discharge of all toxic and harmful pollutants by 1985. The task of the EPA was to develop regulations to meet the provisions of this act and then monitor and enforce those regulations. In order to meet established effluent limitations, industry would be required to apply various levels of water pollution control technology. By July 1, 1977, existing dischargers were to achieve established effluent limitations requiring the application of the best practical pollution control technology (BPT). By July 1, 1983, dischargers were to achieve established effluent limitations requiring the application of the best available technology economically achievable (BAT) to progress reasonably to the national goal of zero discharge of pollutants.

In addition to establishing guidelines for effluent reductions attainable by various levels of technology (BPT and BAT), the EPA also established effluent limitations for toxic pollutants applicable to all dischargers [3]. Nine compounds were designated as toxic pollutants including 2 metals – cadmium and mercury [1].

The regulations for direct dischargers were incorporated into the National Pollutant Discharge Elimination System (NPDES) which was established as the main regulatory system for water pollution control. The EPA has required each state to establish water quality standards that meet or exceed federal water quality standards. These standards provide the basis for source-specific effluent limitations and toxic pollutant limitations. Under the NPDES program each state then has the authority to issue permits for "point-source"* discharges provided that the discharger meets the established federal effluent limitations and toxic pollutant limitations [1].

The EPA was unable to promulgate many of the regulations set forth in the FWPCA Amendments of 1972 in the time specified. Subsequently, in 1976, four suits, brought against the EPA by various environmental groups, were filed to force the agency to establish regulations that would assure that water quality goals would be met. According to the court-upheld "Consent Decree" Settlement Agreement, the EPA agreed to develop and adhere to a scheduled program to establish and enforce BAT effluent limitations, pre-treatment standards,** and new source performance standards (NSPS)*** for 65 "priority" pollutants and classes of pollutants. Thirteen of these are metals and their compounds [3]. In accordance with the Settlement Agreement, 21 industries (or point source categories) would be addressed by these standards.

The Clean Water Act of 1977 incorporated several of the components of the "Consent Decree" Settlement Agreement. This act required that, by July 1, 1984, effluent limitations requiring the application of BAT be achieved for toxic pollutants, including 65 "priority" pollutants and classes of pollutants [3]. Other provisions of the act include a provision that if a POTW removes all or some of a toxic pollutant, the owner of the POTW may adjust the standards applied to the discharger to reflect the final treatment of the POTW. Also in accordance with this act the EPA is required to establish, by July 1, 1984, limitations for conventional pollutant control technology available (BCT)*. It is intended that BCT guidelines replace the more stringent and often more costly BAT guidelines for conventional pollutants after cost and benefit studies, but that BAT guidelines would remain in effect for toxic pollutants. Essentially, with the Clean Water Act of 1977, BAT has become the main source of establishing effluent pollution limitations.

It considers both industrial process controls as well as end line treatment techniques applied by separate treatment facilities. It is meant to establish criteria based on the application of the highest degree of technological pollution control that is feasible and affordable to the industry [4].

In summary, the EPA has required industry to control effluent pollution through various regulations. Industry must monitor effluent discharges and not exceed specified pollutant levels set by NPDES permits. NPDES permit levels are established on the basis of BPT, BAT, and NSPS guidelines. Pretreatment standards apply for effluents to be treated at separate treatment facilities (POTW). For some point-source dischargers the NPDES permits are in the process of review, as BAT guidelines replace the earlier BPT guidelines. Originally, the EPA was to promulgate all major BAT standards by March 1984. Recently the EPA has proposed to extend the deadline for final industrial compliance of BAT standards to July 1, 1988, considering the current July 1, 1984 deadline unobtainable. Other proposals include changes in pretreatment plant regulations, specifically less stringent federal control if local governments have the ability to regulate well run local waste treatment plants. Industry would like to see provisions for modifying the stringent BAT requirements if current controls or modified BAT controls meet water quality criteria.

These controversial proposals have been strongly objected to by environmental groups, particularly the NRDC (National Resources Defense Council). It remains to be seen whether there will be any modification in the regulations of BAT standards or any decentralization of rigid federal regulations of treatment facilities [5]. Meanwhile the EPA's Effluent Guidelines Division in Washington D.C. continues to propose effluent regulations and has established dates for final promulgations of BAT standards for various industries. Within a specified period NPDES permits will reflect the new BAT standards.

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* There are over forty point-source categories addressed by effluent standards. A few include — electroplating, inorganic chemicals manufacturing, petroleum refining, iron and steel manufacturing, paint formulation, plastics and synthetics, grain mills, et al. Among the effluent pollutant regulated, up to 35 different metal pollutants may be addressed by NPDES permits for various industries. Additional industries are regulated at this time by various other federal regulations [1].

** Pretreatment standards for existing sources and new sources (PSES and PSNS) were established to protect publicly owned treatment works (POTW). They apply to waste streams sent to POTW for final treatment and provide protections from materials that might harm the treatment facilities or remain untreated [1].

*** NSPS — New Source performance standards apply to effluent sources where construction began after promulgation of regulations setting standards for that point source category.

* Does not apply to metals but to pH, suspended solids, BOD, COD, fecal coliform, oil and grease.

Hazardous Waste Regulations

A third area of concern was the regulation of pollution from liquid and solid waste. The Resource Conservation and Recovery Act (RCRA) of 1978 is the legislative basis for guidelines for the regulation of pollution of groundwater, surface water, and ambient air from solid waste. For nonhazardous waste, the EPA has established that waste disposal is primarily a local problem and has established guidelines to assist the states in making regulations to protect groundwater and surface water from pollution by liquid and sold waste. The guidelines include consideration of environmentally sensitive areas, air quality, food chain crops, diseases, and safety. Through a series of steps over several years the states are required to survey and evaluate existing disposal sites, and while following federal criteria, develop and periodically review solid waste regulation plans within a specific period following the final promulgation of federal criteria. Federal guidelines will include criteria for design and operation of landfills, leachate control, gas migration control, and groundwater monitoring as well as guidelines for landspreading and surface impoundment of solid wastes [4].

The EPA's main concern is the disposal of hazardous waste, and extensive regulations have been promulgated to control the disposal of hazardous waste. They include control from the point of generation through transportation, storage, and final disposal. The regulations apply to specific substances that are not related to any particular industry. At this time, wastes that are corrosive, reactive, ignitable, or toxic are considered hazardous. But the EPA has proposed that other criteria such as radioactivity, infectiousness and mutagenicity, also be used to determine what constitutes a hazardous waste [1].

A series of test procedures is being developed to define a hazardous waste. One such test is the Extraction Procedure Toxicity Test. The EP Toxicity test was designed to simulate the leaching process in an improperly designed sanitary landfill. It considers toxic constituents that under these conditions would tend to migrate. This test involves an acid extraction procedure in which the representative waste sample is extracted with distilled water maintained at a pH of 5 with acetic acid. If a representative sample contains greater than 0.5% solids it is filtered. The filtrate is saved for later analysis and the solid portion is subjected to the acetic acid extraction. If the sample contains less than 0.5% filterable solids the filtrate is acidifed with acetic acid and analyzed. The solids portion is discarded. A more detailed flow chart is shown in Figure 1.

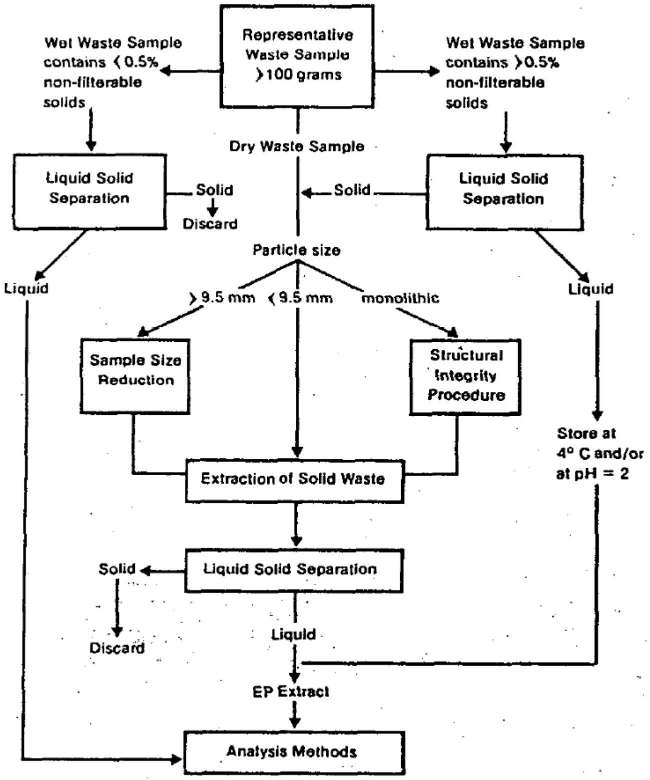

Figure 1. Extraction procedure flowchart.

This flow chart and instructions for the extraction procedure and methods of analysis can be obtained in the US EPA Office of Water and Waste Management publication "Test Methods for Evaluating Solid Waste" [6]. The EP toxicity test included analysis of specific trace elements, pesticides and herbicides. Considering just trace elements, if the values listed in Table 3 are exceeded, the waste exhibits a characteristic of EP toxicity and is considered hazardous [6].

Table 3. Maximum Concentrations for Characteristic of EP Toxicity (mg/L)

Maximum concentrations for characteristic of EP toxicity (mg/L)	
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

At this time, these values are 100 times the National Interim Drinking Water Standards, but will change with revisions of the drinking water standards [1]. Also, proposals have been presented for a distinction to be made between the different valence states of chromium, specifically Cr^{+6} and Cr^{+3}, due to differing toxicities and different migration potentials. There is substantial evidence that hexavalent chromium compounds are carcinogenic in man. Studies with trivalent chromium did not show serious mutagenic potential, in fact trivalent chromium has been shown to have a nutritional function. Also, trivalent chromium salts are virtually insoluble as well as strongly absorbed by inorganic and organic soil materials and therefore have significantly lower migration potentials from a waste disposal area. This is not true for highly soluble hexavalent chromium which can leach out into groundwater. Though this information was known when the present regulations were promulgated there was concern that trivalent chromium would oxidize to the hexavalent form under waste management conditions. Studies indicate that this is unlikely to occur under most waste management systems. But the chlorination treatment of public drinking water may result in the oxidation of trivalent chromium. This is already reflected in the drinking water level. Chromium will remain a toxic pollutant and no changes will be made in drinking water levels [7].

The proposal to amend the characteristic of EP toxicity to include just hexavalent chromium rather than total chromium requires that there be an analytical method to distinguish between the two oxidation states. A method has been developed and is based on the separation of hexavalent chromium from solution by coprecipitation of lead ch.romate with lead sulphate under a controlled pH of 3.5. The precipitate is resolubilized in nitric acid and analyzed by atomic absorption methods. Trivalent chromium does not precipitate under these conditions. This method is being evaluated in various industrial wastes and EP extracts. It is expected that the proposal to amend the characteristic of EP Toxicity for hexavalent chromium will be promulgated after adequate supportive data is obtained [7].

In summary, it is the responsibility of the waste generator to determine whether the waste produced is hazardous. If sufficient quantities of hazardous waste are produced he is responsible for proper disposal according to strict regulatory requirements*. A permit is required for both on-site waste management and transportation to another site for disposal. Proposed regulations contain strict requirements for operation of hazardous waste facilities and long-term monitoring of ground and surface water for contamination. It has been suggested that hazardous waste permits be integrated into the NPDES system. The NPDES system, operated at the state level, would be required to promulgate regulations to meet federal requirements. These regulations would have to be approved by the EPA, but if the states were unable to enforce the regulations, control of hazardous waste would revert back to the EPA [1].

Summary of AA Analysis Methods

Atomic absorption methods are recommended for the determination of metal concentrations, being relatively simple, rapid, and applicable to various types of water and waste samples from drinking water to industrial sludges. Drinking water can usually be analyzed directly, waste water may require pretreatment to solubilize suspended material, and sludges or samples with solid portions may require some type of acid digestion or acid extraction prior to analysis.

Most of the concentrations used to determine "Characteristic of EP Toxicity" (Table 3) can be determined by flame atomic absorption techniques, but analysis at the very low concentrations encountered in the determination of drinking water levels and NPDES permit levels may be difficult if not impossible by flame atomic absorption. Therefore, the more sensitive graphite furnace techniques are part of approved EPA methodology. Other approved methods of analysis include pre-concentration by chelation-extraction procedures, the gaseous hydride method for arsenic and selenium, and the cold vapor technique for mercury. Colorimetric methods have also been approved for some elements. Other instrumental techniques such as emission spectroscopy*, x-ray fluorescence, and anodic stripping are considered as alternate test procedures and must be approved prior to their use [8]. Table 4 summarizes atomic absorption methods for the determination of pollutant metal concentrations at levels established by the National Interim Primary and Secondary Drinking Water Standards.

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* At this time low-volume waste procedures, those generating less than one ton of hazardous waste per month, are not required to comply with the full RCRA regulations. They are allowed to treat or dispose of their wastes on site or send them to an EPA-approved treatment facility. Recently, it has been proposed that this exemption be lowered or eliminated.

* ICP methods of analysis are currently awaiting formal approval for NPDES monitoring. At that time alternate analytical test data showing comparability of results to a currently approved method will not be required [9].

Table 4. Summary of AA Methods

Primary drinking water standards

Element	**Level (mg/L)**	**AA method of analysis**
Arsenic	0.05	Hydride generation or furnace AA
Barium	1.0	Flame or furnace AA
Chromium	0.01	Flame AA with chelaton-extraction or furnace AA
Chromium	0.05	
Lead	0.05	
Mercury	0.02	Cold vapor technique
Selenium	0.01	Hydride generation of furnace AA
Silver	0.05	Flame or furnace AA
Secondary drinking water standards		
Element	Level (mg/L)	AA method of analysis
Copper	1.0	Flame AA
Iron	0.3	
Manganese	0.5	Flame or furnace AA
Zinc	5.0	Flame AA
Proposed drinking water standard		
Sodium	20.0 (mg/L	Flame AA or flame photometry

For hazardous waste regulations the maximum concentrations for "Characteristic of EP Toxicity" listed in Table 3 can be determined by flame atomic absorption except for mercury which would be determined by the cold vapor technique. Depending on the sensitivity of the AA spectrophotometer used it may be preferable to determine the arsenic and selenium by the more sensitive hydride generation method or furnace techniques. If concentrations lower than the maximum allowable need to be accurately quantitated the more sensitive furnace techniques may also be needed for the other elements.

Up to 35 different metals may be regulated at various levels according to individual NPDES permits. Thirteen of these are designed as "priority pollutants" (Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl, and Zn). The NPDES permit levels are based on the federal BAT pollution standards. These standards were established with consideration of the pollutant toxicity, persistence or degradability, effect on organisms in the receiving body of water, the importance of the particular organism, and a reasonable safety margin. The federal water criteria vary by the water type (domestic water supply, irrigation water, freshwater aquatic, marine aquatic), but the maximum allowable effluent levels can be as stringent as the drinking water standards, particularly since the total pollutant discharge over long periods of time is considered. Therefore, determinations of the 13 priority pollutants required to meet NPDES permit levels are often in the µg/L range requiring the most sensitive AA techniques.

Sample Collection and Storage

Prior to sampling the analyst should determine the type of data required — dissolved metals, suspended metals, total concentration or extractable metals. (NPDES permits usually require total metal concentration).

- Dissolved Metals — Sample is filtered through a 0.45 µm membrane filter as soon as possible following collection. The filtrate is acidified with 1:1 NHO_3 to a pH of 2 and analyzed.
- Suspended Metals — Sample is filtered through a 0.45 µm membrane filter. The volume is recorded and the suspended metal concentration is calculated from the determination of the metal concentration on the membrane filter following an acid digestion.
- Total Metals — The entire, unfiltered sample is acidified at time of collection to a pH of 2 with 1:1 NHO_3 acid. A representative aliquot is taken and treated to an acid digest prior to analysis.
- Extractable Metals — The entire sample is heated with HCl and HNO_3 acid and after a specified time and temperature the sample is filtered and analyzed.

Detailed instructions for these procedures can be obtained from the US EPA publications "Methods for Chemical Analysis of Water and Wastes" [8].

Solutions to be analyzed for trace metals can be collected and stored in glass or hard plastic. All liquid samples should be acidified to a pH of $\leq$ 2 with 1:1 HNO_3. The acidified samples can be stored for up to 6 months, except for Hg which should be analyzed within 38 days if stored in glass or within 13 days if stored in plastic [8].

For the determination of trace metals, contamination is a major source of analytical error. There is potential contamination from trace metal impurities in reagents and from laboratory glassware and containers which come in contact with the sample. As well as positive error due to contamination, containers can introduce negative errors by adsorption of metal cations onto the surface of the container. Thus the proper treatment of all apparatus and glassware used in the collection and treatment of the sample is of the utmost importance. Sample containers should be thoroughly washed with a laboratory detergent and tap water, rinsed with nitric acid, and thoroughly rinsed with deionized-distilled water. Any glassware used during the analysis should be cleaned in the same manner. Pipette tips used in manual dispensement of samples in the graphite furnace can also be a source of contamination. They can be cleaned by soaking in 1:5 HNO_3 followed by thorough rinsing with deionized water. The analyst should protect the sample from laboratory dust, another source of contamination. A reagent blank should always be prepared and treated to the same procedures as the sample. Reagent blank concentrations should be subtracted from sample concentration results [8].

Analysis Requirements

Before developing an atomic absorption analysis method the analyst should decide on the degree of accuracy and precision required. If the analysis is to satisfy a regulatory requirement, must he only show that the concentration is below a fixed level or must he quantitate lower levels of the analyte?

The degree of precision required must also be determined—plus or minus 100% or plus or minus 0.1%. The maximum precision obtainable will depend on the method of analysis and the concentration level of the determination. The concentration range of the samples will determine the instrumental techniques as well as measurement methods. The determinations of high concentrations often require a reduction of instrument sensitivity, but determinations near the detection limit require careful instrument optimization and the calculated mean of numerous readings. Alternately, a more sensitive technique may be used.

To help the analyst maintain analytical accuracy, the EPA has established quality control guidelines. The minimum quality control requirements for the analysis of drinking water (NIPDWR) by atomic absorption include [8]:

- All quality control data must be recorded and easily available for inspection.
- Once a year a performance standard must be analyzed and the results must be within a control limit. If not, corrective action must be taken and a follow-up performance standard must be analyzed.

The following requirements must be met daily:

- Calibration curves must be prepared for a reagent blank and a minimum of three standards. Subsequent calibrations must be verified by at least a reagent blank and a standard at or near the maximum allowable concentration level. The standard check must be within ± 10% of the original calibration.
- If more than 20 samples are analyzed per day the calibration curve must be verified by running an additional standard at or near the maximum allowable concentration level every 20 samples. The standard check must be within ± 10% of the original calibration.

Based on knowledge of the regulatory requirements for his particular industry, the analyst can select the proper instrumental method. With the skilful applications of laboratory and instrumental techniques and quality control procedures he can obtain accurate and precise answers satisfying federal and state requirements for regulated pollutant metals.

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