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DETERMINATION OF METALLIC IMPURITIES IN WATER BY ATOMIC ABSORPTION SPECTROMETRY

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DETERMINATION OF METALLIC IMPURITIES IN
WATER BY ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

The technique of atomic absorption spectrometry was studied with a single-beam grating monochromator. The limits of detection of several metals were extended up to 25-fold by increasing the length of the absorbing source, multiple-passing the analytical beam, using fuel-rich flames, varying fuel gases, and/or pumping sample solutions into the flame. The determination of down to 20 to 500 ppb of Fe, Cr, Ni, Co, Mn, and Cu in water was achieved. The coefficient of variation ranged from 4% at 10 to 100 times the limit of detection to 15% at 2 times the limit of detection.

CONTENTS

	<u>Page</u>
Introduction.	5
Summary	5
Discussion	7
Background	7
Experimental Equipment	8
Determination of Lower Concentrations.	9
Future Program	14
Bibliography.	15

LIST OF TABLES AND FIGURES

<u>Table</u>	<u>Page</u>
I Initial Limits of Detection	9
II Accuracy of Determination.	10
III Extended Detectabilities	13
IV Precision of Determinations.	14

<u>Figure</u>		
1 Principle of Atomic Absorption Spectrometry.		7
2 Schematic Diagram of Atomic Absorption Spectrometer		8
3 Multiple-Pass Attachment		11

DETERMINATION OF METALLIC IMPURITIES IN WATER BY ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

Sensitive and precise methods were needed for the determination of part-per-billion concentrations of metallic ions in heavy water moderator for nuclear production reactors. Among the techniques investigated were automated colorimetry, neutron activation analysis, radiochemical analysis, emission spectroscopy, and atomic absorption spectroscopy.

Good "survey" results were obtained by emission spectroscopy, but this technique generally lacked the required precision. Automated colorimetry, neutron activation analysis, and radiochemical analysis gave good results for specific ions, and separate reports on their performance are being issued. No single technique was adequate to determine all required ions.

In a review article Robinson⁽¹⁾ reported detectabilities by atomic absorption spectroscopy for about thirty metals. Detectabilities were approximately equivalent to those from emission spectroscopy, but precision was markedly superior. Coefficients of variation were of the order of 1-2%, which excelled those of emission spectroscopy by factors of 5-25.

This report describes an evaluation of atomic absorption spectroscopy for determining iron, chromium, nickel, cobalt, manganese, and copper in water at part-per-billion concentrations.

SUMMARY

The limits of detection for Fe, Cr, Ni, Co, Mn, and Cu were extended to the point that 2 to 50 ppb of these elements in water can be determined with only a tenfold concentration of a 100-ml sample. The coefficient of variation ranged from 15% near the limit of detection to an average of 4% at concentration levels 10-100 times the limit of detection. Further extension of detectabilities is feasible with improved equipment.

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DISCUSSION

BACKGROUND

The analytical application of atomic absorption spectroscopy, which was first proposed as an analytical technique by Walsh⁽²⁾ in 1955, is based on the fact that metal atoms absorb energy strongly at discrete characteristic wavelengths which coincide with those of the emission spectral lines of the metal. The principle is shown schematically in Figure 1.

FIG. 1 PRINCIPLE OF ATOMIC ABSORPTION SPECTROMETRY

In an analysis, a liquid sample is atomized in a gas flame, where many metallic ions are reduced to neutral atoms. A hollow cathode source of the same metal as that being determined emits the spectrum of the metal to be determined. The beam of light from the hollow cathode traverses the flame and is focused on the slit of a monochromator and readout system, which are set to read the intensity of the chosen spectral line. Light of this wavelength is absorbed by the free unexcited vaporized atoms in the flame, and the amount of absorption is a function of the concentration of the metal.

Metals that are not reduced to the atomic state by the flame are not easily determined by atomic absorption. Aluminum in ordinary fuel-oxygen flames is an example, since conditions favor the formation of aluminum suboxide molecules rather than aluminum atoms.

Many elements emit as well as absorb characteristic light in a flame. In such cases, it is necessary to modulate the light beam emitted by the hollow cathode and to synchronize the detector to the modulation frequency.

It has been demonstrated⁽²⁾ that in a flame the number of atoms in the excited state varies exponentially with the temperature of the flame, and only for flame temperatures greater than 3000°K does the number of excited atoms exceed 1% of the total number of free vaporized atoms. Thus, measurements made by flame emission vary markedly with flame temperature, whereas measurements made by flame absorption are virtually constant with variation in flame temperature up to 3000°, since the number of monatomic vaporized atoms in the ground state is practically the same as the total number of vaporized atoms in the flame.

EXPERIMENTAL EQUIPMENT

An atomic absorption spectrometer was assembled for this work and is shown schematically in Figure 2. No light modulator was included in the original assembly. Elements that emitted light in a flame at very low concentrations, such as sodium, were not studied, and other elements were studied only at concentrations below that at which measurable emission occurred.

FIG. 2 SCHEMATIC DIAGRAM OF ATOMIC ABSORPTION SPECTROMETER

DETERMINATION OF LOWER CONCENTRATIONS

The limits of detection for Fe, Cr, Ni, Co, Mn, and Cu that were reported at the time this work was started are shown in Table I. Initial determinations agreed with these values within a factor of ± 2 . Although copper was not believed to affect corrosion in nuclear reactors, it was utilized extensively in initial studies because copper hollow cathode sources were already available and because copper exhibits one of the lower detectabilities by the technique of atomic absorption.

TABLE 1

Initial Limits of Detection

Element	Detectability Reported, ⁽¹⁾ <u>$\mu\text{g/ml}$</u>	Detectability Found, $\mu\text{g/ml}$
Fe	2.5	5
Cr	10.0	10
Ni	1.0	2
Co	10.0	5
Mn	0.5	1
Cu	0.5	0.5

Since metallic ions were to be determined at concentration levels of a few parts per billion and detectabilities of these cations by atomic absorption spectrometry were at concentration levels of a few parts per million, samples had to be preconcentrated and/or the detectabilities extended to lower concentration levels. Both approaches were examined.

Preconcentration

Seven ppb of iron, copper, and nickel were added to a sample of distilled water. This sample and a sample of the distilled water were concentrated by a factor of 4000 in a "Diamond" Continuous Water Sample Evaporator*. Copper, iron, and nickel were determined by atomic absorption spectrometry. The results, shown in Table II, indicate an accuracy better than 10%.

*A product of Diamond Electronics, Division of Diamond Power Specialty Corporation, Lancaster, Ohio.

TABLE II

Accuracy of Determination

<u>Element</u>	<u>Concentration</u>	
	<u>Original,</u> <u>ppb</u>	<u>Original Plus 7,</u> <u>ppb</u>
Ni	<0.5 ^(a)	6.6
Fe	<1 ^(a)	6.7
Cu	91	99

(a) Not detected.

Extending the Detectabilities

Although satisfactory results were obtained by preconcentration alone, the process for so large a factor as 4000 was long, introduced the possibility of contamination, and was not considered feasible for routine control. Methods of extending detectabilities to lower concentration levels were therefore sought.

Since the attenuation of the signal beam in the flame is proportional to the number of free unexcited vaporized atoms encountered by the signal beam, detectabilities could be extended (1) by increasing the population of free vaporized atoms in the flame and/or (2) by optical maneuvers to increase the number of encounters of the signal beam with free unexcited vaporized atoms in the flame. The following methods of extending the detectabilities were studied:

- Increasing the path length through the absorbing flame.

The path length was increased by placing three Beckman burners in a straight line along the path of the signal beam. In observations with copper, the absorbance by three burners was increased over that by one burner by a factor of only two. The light passing through the flames is not a parallel beam and is at a focus only at the center of the middle flame. In addition, the free atoms are not uniformly distributed throughout the flame. Thus, the beam passing through the two end flames is diffused, and the atoms in those flames interact with a smaller fraction of the beam than do those in the center flame.

The increase in absorbance by three burners, however, effectively lowered the detectability. In addition, the coefficient of variation was improved by a factor of two due to the averaging out of the variations in the sample aspiration rates of the individual burners.

- Passing the signal beam through the absorbing source more than once.

Another technique to achieve increased absorbance was to pass the signal beam through the flame several times. A commercially available assembly of concave mirrors, shown diagrammatically in Figure 3, was employed to pass the beam three or five times through the flame. Although five passes showed more enhancement than three, with some elements the hollow cathode did not give a strong enough signal beam for five passes. Specially designed lamp sources can be used to give stronger signals in routine work and thus extend detectabilities.

The absorbance was enhanced by factors ranging from 2 to 3 for three passes and from 3 to 5 for five passes for various elements. Noncompliance with Lambert's Law is due to the fact that atoms are not uniformly distributed throughout the flame and the beam passes through

FIG. 3 MULTIPLE-PASS ATTACHMENT

the flame at different heights. The distribution of atoms in the flame varies with different elements. Multiple passes did not affect the coefficient of variation.

- Utilizing fuel-rich rather than stoichiometric fuel-oxygen flames.

The utilization of fuel-rich rather than stoichiometric fuel-oxygen flames for the absorbing source increased absorbance. In a stoichiometric fuel-oxygen flame many atoms combine with oxygen to form suboxide molecules. Excess fuel provides a reducing atmosphere that may prevent the combination of atoms with oxygen and/or reduce combined atoms to the free state.⁽⁴⁾ Although a fuel-rich flame exhibits less thermal efficiency in vaporizing atoms, it causes a larger proportion of those vaporized to be reduced to the free state so that there is a net increase in the population of free neutral atoms in the flame. Observations with copper in an oxy-hydrogen flame showed that the amount of excess fuel in the flame was not critical as long as the stoichiometric ratio was exceeded.

- Employing different fuel gases in the absorbing source.

The use of acetylene rather than hydrogen for fuel gas in the absorbing source improved the detectability of some elements. For the elements that were studied, acetylene enhanced absorbance for those above hydrogen in the electromotive series (iron, nickel, cobalt), but did not affect the absorbance of those below hydrogen (silver).

Acetylene cannot be used with all cations of interest because of spectral conflicts. Chromium was such a case. Absorbance is measured at 4255 Å, and a fuel-rich acetylene flame emits a strong background continuum at that wavelength. A modulated or chopped signal beam from the emission source and a synchronized modulated detector readout system could be employed in this and similar cases.

- Pumping the sample into the absorbing flame.

One method of increasing the population of free vaporized atoms in the flame is to introduce more sample solution into the flame by connecting the sample intake tube of the Beckman burner-atomizer to a motor-driven syringe.

The absorbance at the limit of detection for a sample aspirated at about 2 ml/min was increased by a factor of 4 when the sample was injected at a rate of 10 ml/min under the same optical and fuel conditions. At higher rates the enhancement factor decreased, probably due to the cooling effect of introducing a large volume of water rapidly into the flame and thereby reducing its temperature. Precision also suffered from the use of injected samples, the coefficient of variation averaging around 15%. However, since the limit of detection was extended by a factor of 4 beyond that obtained under any other experimental conditions tried, injection will be useful, but it should not be utilized at concentrations high enough to be measured by other techniques.

Detectabilities Achieved

By utilizing multiple passes of the signal beam through the flame in combination with fuel-rich flames, a longer flame path, or increased sample injection, the detectabilities of Fe, Cr, Ni, Co, Mn, and Cu were extended beyond those originally observed by factors of as much as fifty. The detectabilities achieved with existing equipment are shown in Table III. Those that can be extended further with better source lamps are indicated.

TABLE III

Extended Detectabilities

<u>Element</u>	<u>No. of Passes^(a)</u>	<u>Fuel Gas</u>	<u>Detectability, ppb</u>
Fe	3	C ₂ H ₂	200 ^(b)
Cr	3	H ₂	500 ^(b)
Ni	1	C ₂ H ₂	100 ^(b)
Co	3	C ₂ H ₂	200 ^(b)
Mn	3	C ₂ H ₂	50 ^(b)
Cu	5	H ₂	20

(a) Number of passes of beam through flame; see Figure 3 for schematic diagram.

(b) Can be extended with improved source lamps and/or modulated-light detector-amplifier-readout system.

Coefficients of variation are shown in Table IV. These are adequate for most applications of the techniques of atomic absorption.

The results show that Fe, Cr, Ni, Co, Mn, and Cu can be determined in water at the 2 to 50 ppb level with only a tenfold preconcentration. With improved source lamps and a modulated light detecting system, it will be feasible to determine all of these elements at 10 ppb or less with the same degree of preconcentration. With suitable containment facilities the techniques can be applied to the analysis of moderator.

TABLE IV

Precision of Determinations

Element	<u>Aspirated Samples (a)</u>		<u>Pumped Samples (b)</u>	
	<u>Conc. Range, ppm</u>	<u>Coefficient of Variation, %</u>	<u>Conc. Range, ppm</u>	<u>Coefficient of Variation, %</u>
Fe	2-200	5	0.2-2	15
Ni	1-100	5	0.1-1	15
Co	5-500	4	0.2-5	15
Mn	0.5-50	3	0.05-0.5	12
Cu	0.1-10	3	0.02-0.10	15

(a) 3 burners, 6 ml/min.

(b) 1 burner, 10 ml/min.

FUTURE PROGRAM

Existing equipment cannot determine alkali metals because these elements emit light in the absorption flame. Although this objection could be overcome by the addition of a light chopper and modification of the amplifier, a commercial instrument will be procured for further study, since such an instrument will provide also for the employment of improved source lamps and greater facility of routine operation. In addition, a double beam spectrophotometer will enhance precision, since the effects of drift and other variations in the source lamps will be eliminated.

The results of further studies in the application of atomic absorption spectrometry will be presented in subsequent reports.

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