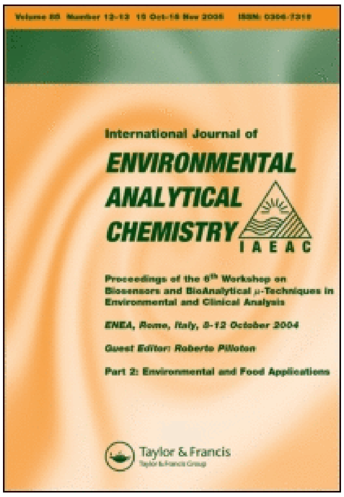


International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A Research Program for Identifying and Measuring Water Pollutants

William T. Donaldson[a]
[a] Southeast Water Laboratory, National Environmental Research Center-Corvallis Environmental Protection Agency, Athens, Georgia, U.S.A.

To cite this Article Donaldson, William T.(1973) 'A Research Program for Identifying and Measuring Water Pollutants', International Journal of Environmental Analytical Chemistry, 3: 1, 1 — 18

To link to this Article: DOI: 10.1080/03067317308071063

URL: http://dx.doi.org/10.1080/03067317308071063

Intern. J. Environ. Anal. Chem., 1973, Vol. 3, pp. 1–18

Printed in Great Britain

A Research Program for Identifying and Measuring Water Pollutants[†]

WILLIAM T. DONALDSON

Southeast Water Laboratory, National Environmental Research Center—
Corvallis Environmental Protection Agency, Athens, Georgia 30601, U.S.A.

(*Received August 23, 1972*)

KEY WORDS: Pollutants, aquatic environment, gas chromatography—mass spectrometry, analytical methods.

Major emphasis in this program is placed on developing systems for identifying all significant pollutants in the aquatic environment instead of following the tradition of developing methods to determine environmental levels of pre-selected pollutants. Gas chromatography-mass spectrometry has been shown to be broadly applicable to identification of organics, and spark source mass spectrometry and neutron activation analysis show promise for elemental analysis.

Highly sensitive and selective methods, such as microwave-induced emission spectrometry, are evaluated for repetitive determination of constituents of known significance. Chemiluminescence and electroanalytical techniques are being investigated for speciation.

Application of methods to the solution of real problems is conducted on a limited scale to bridge the gap between research and broad practical application.

As a regulatory arm of the United States Federal Government, the Environmental Protection Agency (EPA) must have the highest level of competence in identifying and measuring environmental pollutants. Its analytical techniques must be capable of verifying the presence of pollutants and substantiating their concentrations in a broad variety of environmental matrices.

[†] Presented at the Symposium on Recent Advances in the Analytical Chemistry of Pollutants, Halifax, N.S., August 23–25, 1972.

To support both research and enforcement activities in water pollution control, EPA has established the National Water Contaminants Characterization Research Program at the Southeast Water Laboratory. This program, along with one at the Analytical Quality Control Laboratory at Cincinnati, Ohio, is responsible for developing new and improved methods for the identification and measurement of water pollutants.

Recognition that the chemical aspects of water pollution problems can no longer be defined solely by parameters such as biochemical oxygen demand and algal nutrient concentrations challenges the analytical chemist to determine what specific chemicals are present in water and at what concentrations. He must expand the scope of his interest to consider virtually all techniques that may conceivably be applicable to the solution of water pollution problems.

Four critical needs for broader application of available techniques and development of improved techniques are:

1) identification of organic chemical pollutants,
2) qualitative chemical elemental analysis,
3) confirmation of analyses in matrices likely to contain interferences, and
4) speciation of chemical elements.

To attack these problems, the National Water Contaminants Characterization Research Program has assembled a staff of specialists in the fields of organic mass spectrometry, spark source mass spectrometry, molecular spectroscopy, neutron activation analysis, gas-liquid and liquid-liquid chromatography, electroanalytical techniques, chemiluminescence, nuclear magnetic resonance spectroscopy, and emission spectrometry. This staff not only conducts an in-house experimental program, but also reviews and monitors extramural grants and contracts that are an integral part of the program. This arrangement is highly advantageous in keeping the staff abreast of new methodology developed by extramural researchers and in giving extramural researchers a better appreciation for the Agency's needs. In-house and extramural funds for the program are approximately equal.

Once a research objective is defined, a decision is made whether the task should be achieved in-house or extramurally. In general, new techniques are first considered by extramural researchers; when a technique shows promise, an in-house project is begun. Techniques nearing broad application must move in-house if the dangerous gap between the extramural researcher and the applied analytical chemist is to be bridged. Most analytical support groups in other research programs and field survey teams also do limited (and sometimes extensive) "development work" to adapt techniques to their specialized needs. Such development work is done better by those support groups and the

Contaminants Characterization Program does not normally perform these tasks.

IDENTIFICATION OF ORGANIC CHEMICAL POLLUTANTS

Of the 10 to 100 thousand organic chemicals that find their way into lakes and streams, less than one thousand had been identified by the end of 1971. Because of the large number of compounds and because some of these compounds are known to be toxic to aquatic organisms at concentrations as low as 10 to 100 ng/l, identification techniques must be highly specific and sensitive. The increasing tendency to set effluent water quality standards indicates the need for the capability in every EPA regional and major research laboratory to identify organic pollutants.

After three years of evaluating gas chromatography-mass spectrometry (GC-MS) with the Perkin Elmer RMU-7 mass spectrometer at the Southeast Water Laboratory,[1] GC-MS with computerized data reduction and a computer program for identification by empirical spectra matching was selected in 1971 as the best single technique for identifying moderately volatile organic compounds. Desired spectrometer characteristics included ease of operation and maintenance when interfaced with a gas chromatograph. Resolution easily maintained above 600 amu was deemed to be adequate for low-resolution spectra-matching. A high priority was placed on computerized data reduction.

A computerized spectra-matching program was jointly developed with Battelle Columbus Laboratories. Operating under an EPA research grant, Hoyland and Neher[2] at Battelle modified the algorithm and abbreviated spectrum scheme of Hertz *et al.*[3] for use with a CDC 6400 computer. An initial library of approx. 11,000 spectra from the Aldermaston file is being supplemented by spectra of compounds identified in actual wastewaters.[4] This computerized spectra matching is available to support the 15 GC-MS-computer systems in EPA laboratories across the country.

A typical procedure for identifying organic compounds in wastewater involves extraction with a non-polar solvent such as chloroform or hexane. Extracts are concentrated and 1–10 mcl aliquots of the concentrate are injected into the GC-MS. At the Southeast Water Laboratory, a Finnigan model 1015 quadrupole mass spectrometer with a System Industries data system is in use. The computer directs the mass spectrometer to scan the GC effluent every 3 sec and stores total ion current data and corresponding mass spectra on magnetic tape. At the end of a GC-MS run, the computer retrieves this ion current information and plots it as a reconstructed gas chromatogram (RGC). A typical RGC is shown in Figure 1; the numbers of the abscissa correspond to the mass spectra stored on tape.

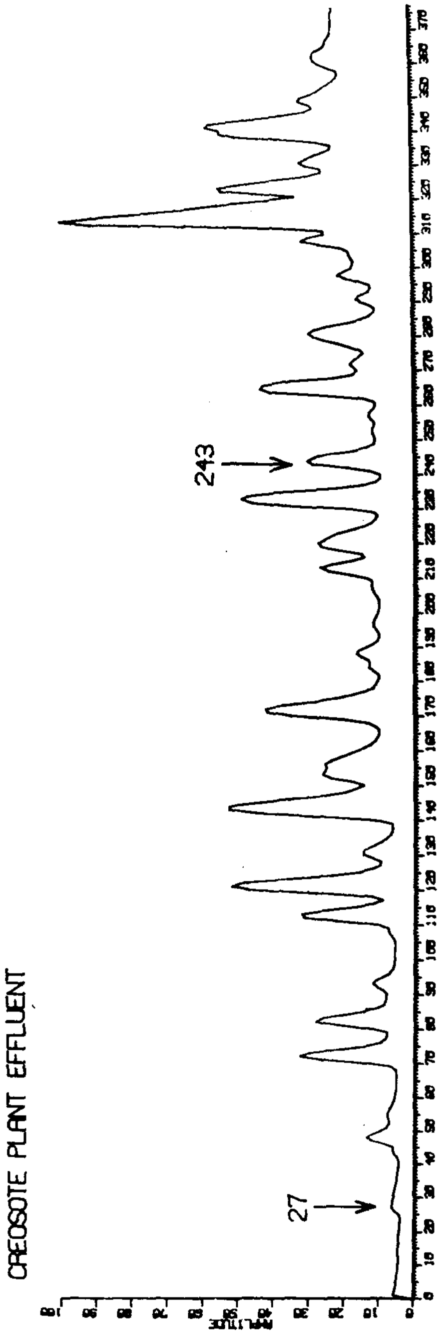


FIGURE 1 Reconstructed gas chromatogram of industrial waste effluent.

This RGC represents an industrial waste effluent sampled and analyzed by the Surveillance and Analysis Division of EPA's Region IV using the technique described above. Eighteen organic compounds were identified in this sample within 8 hr after injection into the GC-MS. The compound represented by mass spectrum No. 27 probably comprised less than 10 ng of the estimated 10 to 100 mcg of extract injected. A satisfactory mass spectrum was obtained, however, and the computer identified it as that of 2,4-dimethylpyridine (Figure 2). Comparison with a spectrum of pure 2,4-dimethylpyridine (Figure 3) confirmed the computer's identification.

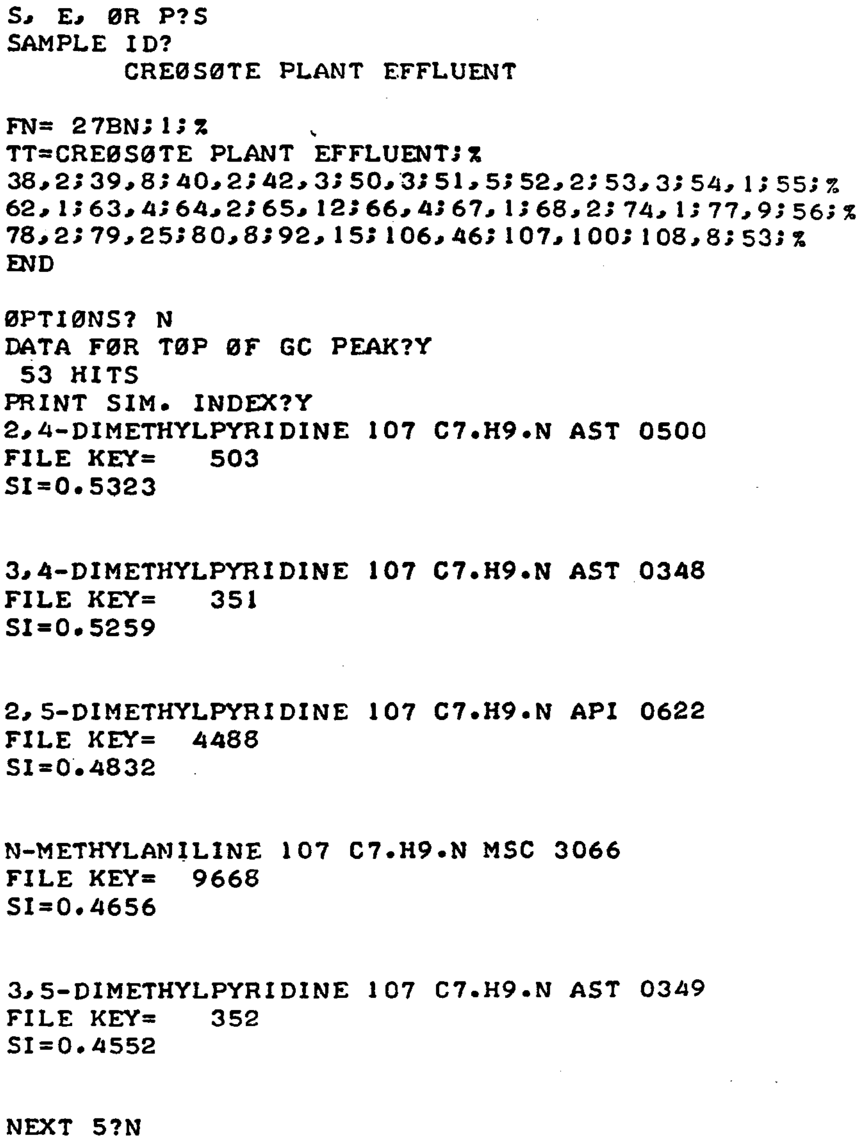
Spectrum No. 243 (Figure 1) was identified by the computer as dibenzofuran (Figure 4). Note that the last term, S.I. (Similarity Index), is a numerical index (ranging between zero and one) of the relationship between (1) the average ratio of corresponding peak intensities in the unknown and in the reference and (2) the fraction of unmatched peaks contained in both spectra. It serves as a measure of the resemblance of the unknown spectrum to a stored spectrum. The indices for three different file spectra of dibenzofuran are significantly higher than the next highest index. The spectrum of pure dibenzofuran confirmed its identity (Figure 5). The compounds identified in this sample are listed in Table I. Several are reported to be carcinogenic; others are known to cause taste problems in both water and fish flesh.

A Fourier transform infrared spectrometer interfaced with a gas chromatograph is being investigated as a means of confirming mass spectral identifications by comparing unknown infrared spectra with those in a computerized infrared spectra library. This confirmation will eliminate the need to locate or synthesize pure compounds to confirm identities. Fourier transform infrared will also help identify compounds whose spectra are not yet in the computerized mass spectra library, which is still relatively small compared to the 100,000-compound infrared spectra files.

When enough sample is available, n.m.r. spectroscopy is used to elucidate structures of unknown compounds. Improvement of n.m.r. sensitivity through use of microprobes and Fourier transform techniques is planned as an extramural project. Laser Raman spectroscopy and phosphorescence will also be investigated extramurally. Other extramural projects will develop a deductive computer program for mass spectra analysis and further investigate the value of high-resolution mass spectrometry.

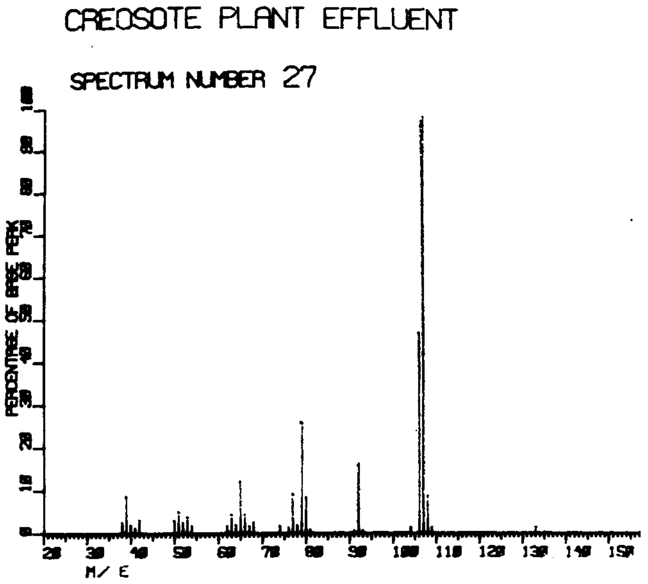
An in-house project is the investigation of the mass chromatograph, which uses the gas density principle to determine the molecular weight of compounds in GC effluents. Compilation of a retention time-molecular weight index may permit a substantial number of tentative identifications of pollutants at low cost.

Two other in-house projects involve characterization of industrial and municipal wastewaters. As specific identities of chemicals in these wastes are



```
S, E, ØR P?S
SAMPLE ID?
       CREØSØTE PLANT EFFLUENT

FN= 27BN;1;%
TT=CREØSØTE PLANT EFFLUENT;%
38,2;39,8;40,2;42,3;50,3;51,5;52,2;53,3;54,1;55;%
62,1;63,4;64,2;65,12;66,4;67,1;68,2;74,1;77,9;56;%
78,2;79,25;80,8;92,15;106,46;107,100;108,8;53;%
END

ØPTIØNS? N
DATA FØR TØP ØF GC PEAK?Y
 53 HITS
PRINT SIM. INDEX?Y
2,4-DIMETHYLPYRIDINE 107 C7.H9.N AST 0500
FILE KEY=   503
SI=0.5323


3,4-DIMETHYLPYRIDINE 107 C7.H9.N AST 0348
FILE KEY=   351
SI=0.5259


2,5-DIMETHYLPYRIDINE 107 C7.H9.N API 0622
FILE KEY=  4488
SI=0.4832


N-METHYLANILINE 107 C7.H9.N MSC 3066
FILE KEY=  9668
SI=0.4656


3,5-DIMETHYLPYRIDINE 107 C7.H9.N AST 0349
FILE KEY=   352
SI=0.4552


NEXT 5?N
```

FIGURE 2 Computer identification of compound producing spectrum No. 27.



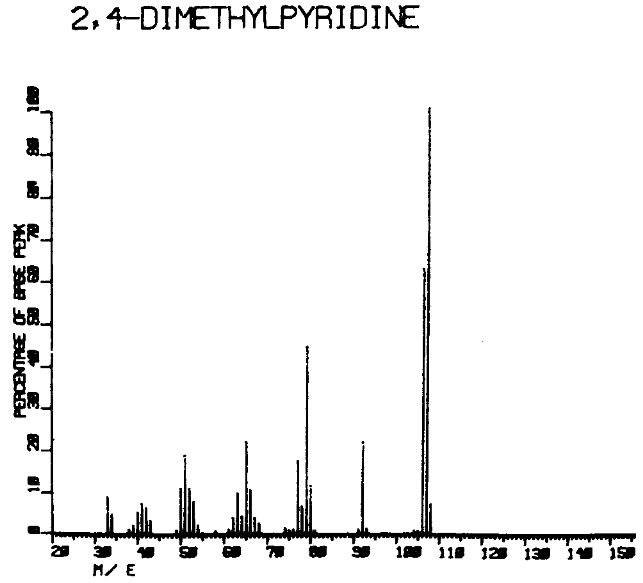
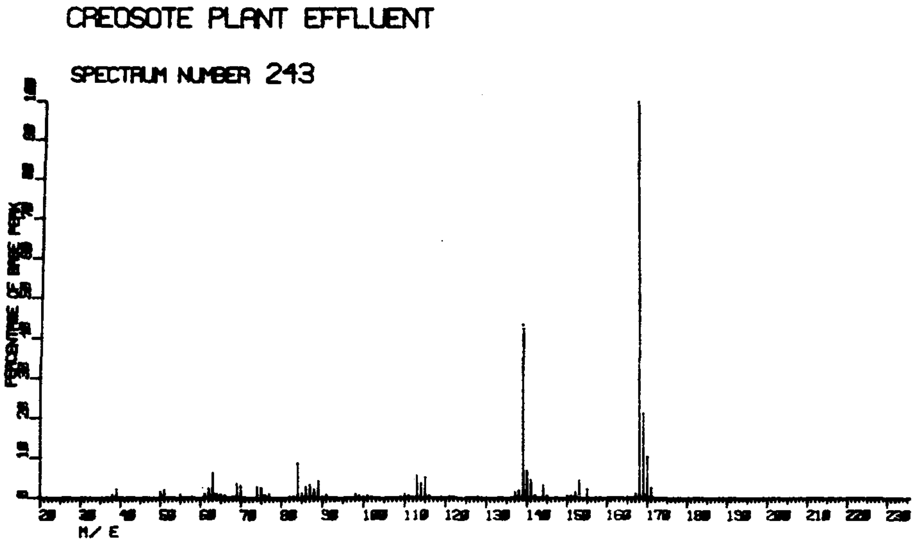


FIGURE 3 Comparison of spectrum of pure 2, 4-dimethylpyridine with spectrum No. 27

```
S, E, 0R P?S
SAMPLE ID?
        CRE0S0TE PLANT EFFLUENT

FN= 243BN;1;%
TT= CRE0S0TE PLANT EFFLUENT;%
39,2;50,1;51,2;62,2;63,6;69,3;70,3;74,2;75,2;55;%
34,8;86,2;87,3;88,2;89,4;113,5;114,3;115,5;137,1;61;%
138,2;139,43;140,6;141,4;144,3;152,1;153,4;155,2;168,100;71;%
169,21;170,10;171,2;24;%
ND

PTI0NS? N
ATA F0R T0P 0F GC PEAK?Y
 18 HITS
RINT SIM. INDEX?Y
IBENZ0(BD)FURAN (DIPHENYLENE 0XIDE) 168 C12.H8.0 TRC 0101
ILE KEY=  6425
I=0.4777


IBENZ0FURAN (DIPHENYLENE 0XIDF) 168 C12.H8.0 API 0633
ILE KEY=  4499
I=0.4269


IBENZ0FURAN 168 C12.H8.0 D0W 1137
ILE KEY=  3036
I=0.4125


-(3\,5\-DIMETH0XYPHENYL)-1-HYDR0XY-3-METHYLBUTANF 224 C13.H20.03 MSC
546
ILE KEY=  9150
I=0.1955


-AMIN0-5-CHL0R0BENZ0XAZ0LE                    (Z0XAZ0LAMINE) 168 C7.H5.
2,0.CL MSC 3781
ILE KEY= 10382
I=0.1772


EXT 5?N
```

FIGURE 4 Computer identification of compound producing spectrum No. 243.



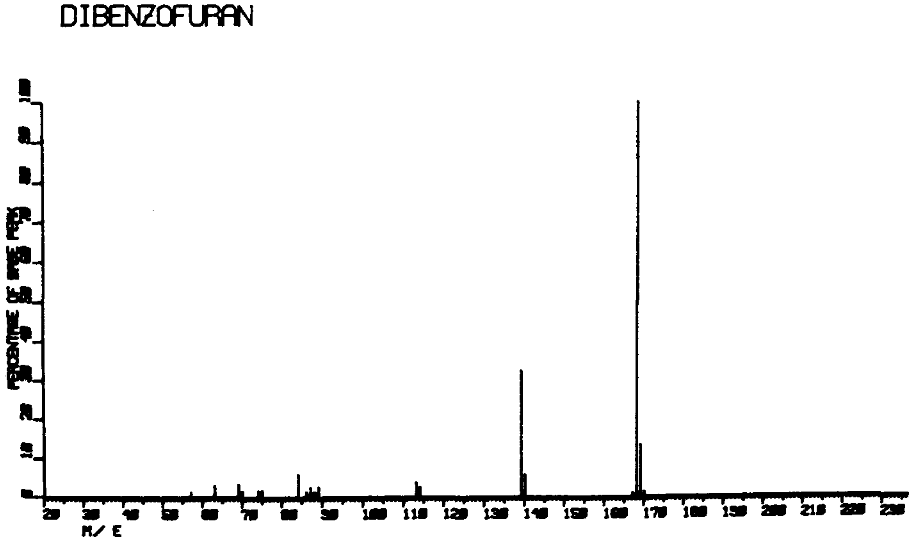


FIGURE 5 Comparison of spectrum of pure dibenzofuran with spectrum No. 243.

established, their mass spectra will be added to the computer library, and they will be reported to other EPA research groups concerned with the fate, effects and control of water pollutants.[5,6]

TABLE I

Compounds identified in creosote plant effluent

Dimethyl pyridine	Dimethyl quinoline
Phenol	Biphenyl
Trimethyl pyridines	Dibenzofuran
Cresols	Fluorene
Xylenols	Dibenzothiophene
Quinoline	Carbazole
Iso-quinoline	Anthraquinone
Trimethyl phenol	Methyl pyrenes
Methyl quinoline	Phenanthrene

CHEMICAL ELEMENTAL ANALYSIS

A knowledge of all of the chemical elements present in water or sediments is extremely valuable in diagnosing the cause of pollution problems. Currently most elemental determinations are made for only selected elements by techniques, such as atomic absorption, that consider only one element at a time. A method for simultaneously determining all elements present above a concentration of 1 mcg/l is needed.

Spark source mass spectrometry shows significant promise as a scouting technique. Theoretically all chemical elements in any matrix can be identified and measured with the spark source mass spectrometer, provided organic materials in the sample have been reduced to their elemental components (other than carbon, hydrogen, and oxygen). The sensitivity of the spark source mass spectrometer allows measurement of elements at concentrations less than 1 mcg/l in a 100-ml sample of water.

At the Southeast Water Laboratory we are evaluating the spark source mass spectrometer's use in combined qualitative—semi-quantitative analysis of water. The electrical detection system of the AEI MS-702 mass spectrometer is interfaced with a DEC PDP-8/E computer. The computer program converts the electronic signal from the detector to a typed listing of all elements present and their concentrations in micrograms per liter.

Spark source mass spectrometric analysis of a standard aqueous solution containing 22 elements gave coefficients of variation of 14–50%[7] for different elements. Precision for an unfiltered lake-water sample was somewhat poorer,

TABLE II

Spark source mass spectrometric analysis of unfiltered lake water
(mcg/l)

Element	Sr	Br	Fe	Mn	P	Ni	Co	Pb	Ce	Cr	As	Co	U	Sn	Sn	Ba	Ba	Cu	Cu	Cu
Attenuation	1	1	1	1	1	2	2	3	3	3	3	3		2	3	1	2	1	2	3
Run No.																				
1						13.3	13.5	8.2	1.9	18.0	11.0	27.2	3.5	17.6		157	318		10.3	15.5
2	1237	12.0	2775	153	60	29.5	13.5	8.6	2.6	24.2		25.2		18.7	18.6	230	297	13.0	14.7	13.2
4						21.0	19.4							18.0			187		17.7	
5	2945	9.4	4107	194	102	35.2	24.1	9.1	1.8			25.4		26.3	12.4	124		7.1	27.4	25.0
8	4196		7562	223	151	43.0	27.4	2.3	2.7	52.3	11.7	24.5	1.7	50.4	14.5	179	262		19.3	9.5
9	5363	14.1	7668	339	174	24.2	18.4	1.3	1.3	50.8	2.5	22.3		31.2	29.9	86	104	14.1	11.5	15.4
10			6294	163	158	41.1		2.5	1.0	36.5	1.7	15.0			19.2	274	400		21.4	15.0

as expected, but the ability to analyze elements whose concentrations spanned three orders of magnitude in a single sample was demonstrated. Table II lists data for 16 elements from seven different analyses. Each analysis was performed at three different signal attenuations to cover the broad range of concentrations. Only data from the optimum attenuation are given, except for barium, tin, and copper. The data indicate that these three elements could have been determined with similar precision and accuracy at two or three attenuations.

Figure 6 shows the computer printout for run No. 9, which was made at the middle attenuation. Note that doubly and triply charged ions and the presence of confirming isotopes are recorded. The doubly charged ions of lead and chromium were not detected at this attenuation, but they were at the lowest (No. 1) attenuation. Doubly charged ions for elements below mass 34 were not detected because the scan was purposely stopped at mass 19.

In 1970 the Southeast Water Laboratory established a laboratory at the Nuclear Research Center at the Georgia Institute of Technology to apply neutron activation analysis to water and sediments. Neutron activation is particularly useful in performing multi-element determinations for large numbers of samples. In the analysis of bottom sediment samples taken from 17 different locations through the country, 43 elements were detected and measured by performing two irradiations and three gamma-pulse-height analyses for each sample.[8] If a multi-purpose experimental reactor is used, neutron activation analysis costs less than $10 per element for samples containing 20–40 elements. The costs of spark source mass spectrometric analyses are similar.

Techniques under consideration for replicate determinations of 1–30 elements are microwave-excited emission spectrometry, flameless atomic absorption spectrometry, and X-ray emission spectrometry.

Confirmation of Analyses

The results of colorimetric, emission and absorption techniques may be inaccurate, unless the analyst has a thorough knowledge of all possible interfering constituents in the sample. Such knowledge of waste samples and receiving streams is rare. These atomic techniques are dependent on transformation of energy or exchanges of electrons that occur outside the nucleus of the atom. Techniques related to nuclear properties can confirm analyses performed with techniques based on atomic properties since interferences would be of an entirely different nature for the two types of techniques. Confirmatory analysis appears to be the solution to the problem of not knowing what interferences are present.

Table III shows a comparison of neutron activation and spark source mass

```
- - -
MARION9X

MASS  ELEMENT          PPB        ++?    CONFIRM    CHECK     COMPLEX
                      WEIGHT      +++?   ISOTOPES   OVERLAP    IONS


 208  LEAD                 1.63    NO        NO
 138  BARIUM             103.68    2+       YES
 118  TIN                 31.20    NO       YES
 111  CADMIUM              6.21    NO       YES
  89  YTTRIUM       STANDARD
  88  STRONTIUM          577.47    3+       YES
  79  BROMINE              3.45    2+       YES
  75  ARSENIC             24.26    2+        -
  70  GERMANIUM           43.48    NO        NO
  69  GALLIUM             23.10    2+        NO                   C40H(   69)
  66  ZINC               556.45    2+       YES                   C4N (   66)
                                                                  C40 (   68)
                                                                  C40 (   64)
                                                                  C4C (   64)
  63  COPPER              11.48    2+        NO                   C40H(   65)
  58  NICKEL              24.20    NO       YES                   C4N (   62)
  59  COBALT              18.44    2+        -
  56  IRON               345.58    3+       YES                   C30H(   56)
  55  MANGANESE          200.30    2+        -                    C30 (   55)
  52  CHROMIUM           168.91    NO        NO                   C30 (   52)
                                                                  C4  (   52)
                                                                  C30H(   53)
                                                                  C3N (   53)
                                                                  C4H (   53)
  51  VANADIUM             8.41    2+        -                    C3C (   51)
  47  TITANIUM            39.33    2+        NO
  45  SCANDIUM            15.58    2+        -
  40  CALCIUM            411.76    2+       YES                   C20 (   40)
                                                                  C2N (   40)
                                                                  C3H (   40)
                                                                  C20H(   43)
  39  POTASSIUM          283.27    2+        NO                   C3  (   39)
                                                                  C20H(   41)
  35  CHLORINE           242.73    2+        NO                   C3H (   37)
  34  SULPHUR           4183.27    NO        NO
  31  PHOSPHORUS         107.41    NO        -
  28  SILICON            233.45    NO        NO                   CO (   28)
                                                                  COH(   29)
                                                                  CO (   29)
                                                                  COH(   30)
  27  ALUMINIUM          156.14    NO        -                    CN (   27)
                                                                  C2H (   27)
  23  SODIUM             312.43    NO        -
  19  FLUORINE             7.30    NO        -      57(   19)

                            END OF RUN

ACCEPT ? :Y
```

FIGURE 6 Computer printout of spark source mass spectrometric analysis of lake water.

spectrometry for the preliminary determination of arsenic in both water and sediments from a stream receiving an industrial effluent. Other methods had produced widely varying results. Since these two methods showed general agreement for these selected samples, the remaining samples were analyzed more precisely by neutron activation analysis alone. Data for one group of samples are shown in Table IV. Note that even though concentrations vary by a factor of about 500, precision of triplicate determinations is acceptable.

TABLE III

Comparison of neutron activation and mass spectrometric analyses for arsenic

Sample No.	Neutron activation	Mass spectrometry
	Water samples (mg/l)	
1	2×10^{-1}	1×10^{-1}
2	$< 1\times10^{-3}$	1×10^{-4}
3	1.6	0.9
	Residue samples (mg/kg)	
1	10	10
2	66	20
3	2.2×10^{3}	3×10^{3}

TABLE IV

Replicate determination for arsenic in residues by neutron activation analysis

	Arsenic (mg/kg)		
Sample No.	Aliquot 1	Aliquot 2	Aliquot 3
1	4.35×10^{3}	4.02×10^{3}	3.73×10^{3}
2	6.18×10^{2}	7.89×10^{2}	6.71×10^{2}
3	8.23×10^{2}	6.89×10^{2}	8.31×10^{2}
4	2.93×10^{3}	3.27×10^{3}	4.26×10^{3}
5	8.23	10.01	9.61
6	2.02×10^{1}	2.06×10^{1}	2.05×10^{1}
7	3.99×10^{3}	3.60×10^{3}	3.98×10^{3}
8	6.98×10^{2}	7.09×10^{2}	7.29×10^{2}
9	2.36×10^{3}	2.23×10^{3}	2.88×10^{3}
10	2.20×10^{3}	2.07×10^{3}	2.11×10^{3}

Speciation of chemical elements

Although many water quality criteria for chemical elements are based on total elemental concentration in water, knowledge of the elemental species present permits determination of toxicity and other environmental effects. For example, copper in the cupric ion state is more toxic to some fish than when it is complexed, and the toxicity of chromium(III) is different from that of chromium(VI).

Pulsed polarography permits the determination of various ions in the 10 mcg/l range. Figure 7 shows pulsed differential polarograms of 1 mg

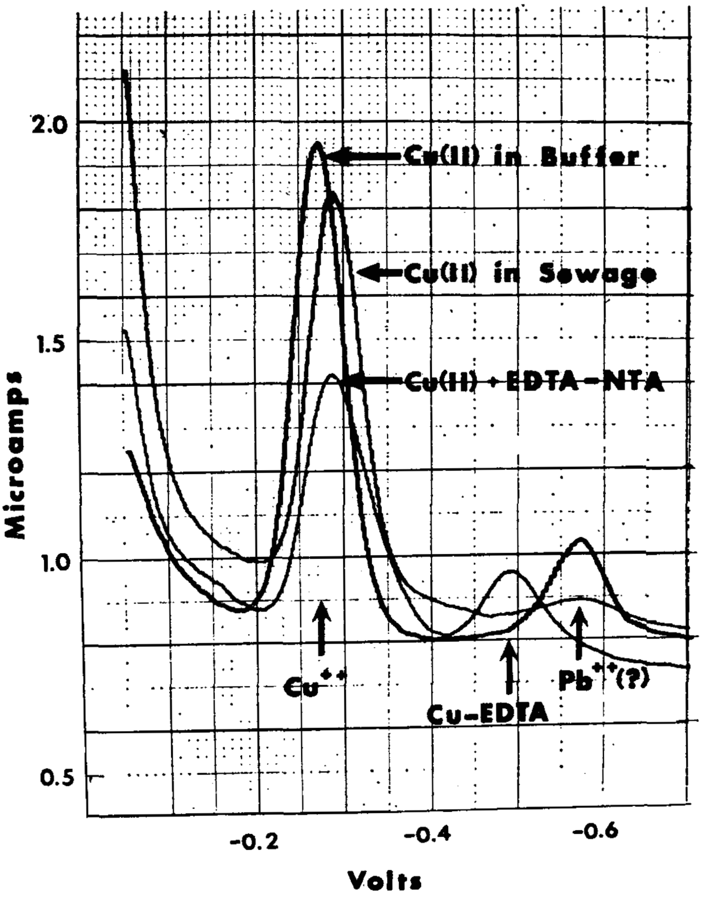


FIGURE 7 Pulsed differential polarogram of Cu(II) showing effect of complexing agents on Cu(II) concentration.

Cu(II)/l in buffer solution, 1 mg Cu(II)/l in a mixture of 60% buffer—40% effluent of domestic sewage from secondary treatment, and 1 mg Cu(II)/l with 5×10^{-6}M NTA and 5×10^{-6} EDTA. The sewage apparently reduced the concentration of Cu(II). It also reduced the concentration of the element or complex responsible for the peak at −0.6 V (probably lead). As would be expected, EDTA and NTA reduced the Cu(II) concentration substantially, and the Cu-EDTA complex peaks at 0.49 V.

Chemiluminescence shows promise for speciation of some metals. Free Cr(III) can be distinguished from complexed Cr(III) and Cr(VI) by a method developed at the Southeast Water Laboratory.[9] The difference in response between 10^{-3}M Cr(III) in complexed and uncomplexed forms is illustrated in Table V. Table VI shows precision of the chemiluminescence method for Cr(III) in natural waters containing 1 to 10 mcg Cr(III)/l.

TABLE V

Effect of complexing agents on Cr(III) catalysis of luminol oxidation

Catalyst	Relative intensity
Uncomplexed Cr(III)	100
Cr(III)—glycine	8
Cr(III)—citrate	0
Cr(III)—tartrate	3
Cr(III)—2,4-pentanedione	5

TABLE VI

Chromium(III) analysis of natural water samples

Sample	Cr(III) (mcg/l)
Oconee River	1.3
	1.6
	2.1
Lake Lanier	1.0
	1.1
	1.0
Tap water	9.4
	9.9
	10.4
Oxidation Pond	4.2
	5.2
	5.7

Extramurally, ion selective electrodes are being developed using a new liquid membrane electrode, and an ion-electrode method was developed to determine NTA in the presence of phosphate and sulfate. Also extramurally, an attempt is being made to develop an enzyme electrode that is specific for orthophosphate at the 10 mcg/l–10 mg/l range.

CONCLUSIONS

Applicability to water pollution abatement has been demonstrated for a significant number of advanced analytical techniques, but until these techniques are applied broadly their value will not be realized. Our research program is devoted to bridging the gap between fundamental development and practical application in the laboratories of the EPA. We believe that exploitation of better chemical analysis will provide the key to dramatic progress in water pollution control.

Acknowledgement

The GC–MS analysis of creosote plant effluent was performed by William Loy and Donald Brown of EPA's Region IV Surveillance and Analysis Division at the Southeast Water Laboratory.

Disclaimer

Mention in this paper of trade names or commercial products does not constitute the Environmental Protection Agency's endorsement or recommendation for use.

References

1. A. W. Garrison, L. H. Keith, and M. M. Walker, Presented at the 18th Annual Conference on Mass Spectrometry and Allied Topics, San Francisco, Calif. (June 1970).
2. J. R. Hoyland and M. B. Neher, *Implementation of a Computer-based Information System for Mass Spectral Identification of Pesticides*, 3rd Quarterly Report, EPA Research Grant 16020 HGD (1972).
3. H. S. Hertz, R. A. Hites, and K. Biemann, *Anal. Chem.* 43, 681 (1971).
4. J. M. McGuire, A. L. Alford, and M. H. Carter, Presented at the American Society for Mass Spectrometry's Twentieth Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas (June 4–9, 1972).
5. L. H. Keith, Presented at the Division of Water, Air, and Waste Chemisty, American Chemical Society Meeting, Boston, Mass. (April 1972).
6. A. W. Garrison, Presented at the American Chemical Society Meeting, New York, N.Y. (Sept. 1969).
7. C. E. Taylor, W. H. McDaniel, and J. M. McGuire, Presented at the American Society for Mass Spectrometry's Twentieth Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas (June 4–9, 1972).

8. R. V. Moore and O. W. Propheter, *Neutron Activation Analysis of Bottom Sediments*, Environmental Protection Agency, EPA-R2-72-009, in press.
9. W. R. Seitz, W. W. Suydam, and D. M. Hercules, *Anal. Chem.* **44**, 957 (1972).