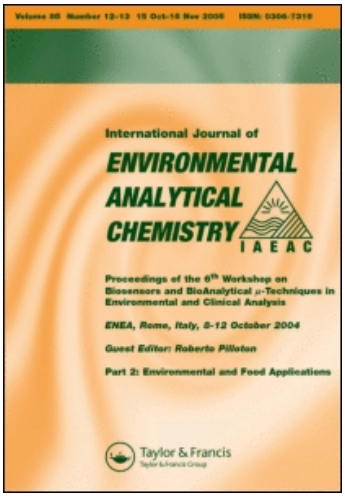

International Journal of Environmental Analytical Chemistry

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

Chemiluminescence Analysis for Trace Pollutants

W. Rudolf Seitz[a]; David M. Hercules[b]
[a] National Environmental Research Center, Corvallis, Environmental Protection Agency, Athens, Georgia, U.S.A. [b] Department of Chemistry, University of Georgia, Athens, Georgia, U.S.A.

To cite this Article Seitz, W. Rudolf and Hercules, David M.(1973) 'Chemiluminescence Analysis for Trace Pollutants', International Journal of Environmental Analytical Chemistry, 2: 4, 273 — 290
To link to this Article: DOI: 10.1080/03067317308076397
URL: http://dx.doi.org/10.1080/03067317308076397

Intern. J. Environ. Anal. Chem., 1973, Vol. 2, pp. 273–290

Printed in Great Britain

Chemiluminescence Analysis for Trace Pollutants†

W. RUDOLF SEITZ

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

and

DAVID M. HERCULES

Department of Chemistry, University of Georgia, Athens, Georgia 30601, U.S.A.

(*Received August 23, 1972*)

KEY WORDS: Chemiluminescence, trace metals, iron, chromium, luminol.

The sensitivity of luminol chemiluminescence to small catalyst concentrations can be exploited for environmental analysis in several ways. Selective methods for Cr(III) and Fe(II) in complex solutions have been applied to natural samples. The detection limits are 0.03 mcg/l and 0.005 mcg/l, respectively.

Species that do not catalyze luminol chemiluminescence can be determined by titration with reagents that catalyze the reaction. For example, arsenic and aqueous sulfur dioxide can be titrated with iodine, an efficient catalyst. MnO_4^-, OCl^-, V(II), and Cr(II) are other catalysts that can be used as titrants.

Preliminary ion exchange separation in concentrated LiCl solutions extends chemiluminescence to other catalysts of the luminol reaction: Ni(II), Co(II), Mn(II), Cu(II), and V(IV).

INTRODUCTION

Because some chemicals are significant pollutants at parts-per-billion concentrations or lower, analytical chemists have expended considerable effort to increase the sensitivity of established methods and to develop new methodologies having sufficient sensitivity to analyze for trace pollutants without elaborate and error-prone preconcentration techniques. One new

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

approach is chemiluminescence analysis, based on catalysis of the luminol reaction. Several metal ions catalyze the oxidation of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) by hydrogen peroxide in basic aqueous solution. This extensively studied reaction is one of the most efficient chemiluminescent reactions known.[1-3] A few catalysts are effective even in the absence of hydrogen peroxide.

In the presence of excess reagents, the intensity of light emission is proportional to catalyst concentration, a relationship that can be used for trace analysis. Babko and co-workers [4-7] reported methods for cobalt, copper, and iron, all based on catalysis of the luminol reaction. By simply mixing the reactants while exposing the container to a photographic film and measuring exposure as a function of concentration, they found detection limits of 1, 3, and 10 ppb for cobalt, copper, and iron, respectively. Recently Seitz *et al.*[8] reported a specific method for Cr(III), having even greater sensitivity (ca. 25 parts per trillion).

The luminol reaction and apparatus described in Ref. 8 can be applied to a number of environmental problems.

EXPERIMENTAL

Apparatus

The chemiluminescence apparatus has been described in detail elsewhere.[8,9]

Chemicals

Luminol from Eastman Organic Chemicals (Eastman Kodak Co., Rochester, N.Y.) was converted to the sodium salt and was purified by recrystallization from basic aqueous solution.

The purified sodium luminol was dissolved in 0.1M KOH–H_3BO_3 buffer to control the pH in the reaction cell. The H_3BO_3 concentration was kept constant while the amount of KOH was varied to achieve the desired pH.

All reagents were prepared using water from a Continental Water Conditioning Company deionization system.

Standard 0.100M catalyst solutions were prepared by weighing. Other standards were prepared by dilution.

ANALYTICAL CHARACTERISTICS OF THE LUMINOL REACTION

Catalysts

Table I lists metal ions that catalyze the luminol reaction only in the presence of peroxide, along with some of their analytical characteristics. There are

probably several more metal ions, not included in this table, that are also catalysts of luminol chemiluminescence.

The detection limits of Table I show why chemiluminescence analysis is of interest. They are much lower than for most other methods. In fact, sensitivity is so great that in some situations it can be reduced in return for some other benefit, e.g. dilution to eliminate an interference. Unlike other techniques where a great deal of research goes into extending sensitivity, the problems in chemiluminescence analysis are associated with determining one element specifically in a complex sample. Because all catalysts produce the same output, i.e. luminol chemiluminescence, resolution must be based on differences in the chemistry of various catalysts.

TABLE I

Catalysts in the presence of peroxide

Catalyst	Approximate detection limit (M)	Linear range (M)	Remarks
Co(II)	10^{-11}	10^{-11} to 10^{-7}	—
Cu(II)	10^{-9}	10^{-9} to 10^{-6}	in NH_3 for linearity
Ni(II)	10^{-8}	10^{-8} to 10^{-5}	—
Cr(III)	10^{-9}	10^{-9} to 10^{-6}	—
V(IV)	—	—	quite sensitive
Mn(II)	10^{-8}	—	requires amines

The limiting factor that determines detection limits is light emission from H_2O_2 and luminol buffer in the absence of added catalysts. We believe this background light is catalyzed by trace metal contaminants in the reagents. If this explanation of the background light is correct, it should be possible to reduce detection limits by purifying the H_2O_2 and luminol buffer before making measurements. This has not yet been attempted.

Cu(II) and Mn(II) behave differently from other catalysts. In a non-complexing medium, chemiluminescence versus copper curves are non-linear at higher copper concentrations ($> 10^{-7}$M Cu). Chemiluminescence per standard addition of Cu(II) increases as Cu(II) concentration increases. Peaks on our apparatus are poorly defined and less reproducible than for other catalysts. In the presence of ammonia (and amines), the response becomes linear up to higher concentrations and peaks are well defined. Mn(II) does not catalyze chemiluminescence in water without complexing agents, but in the presence of amines it is activated as a catalyst.

Table II lists catalysts of the luminol reaction in the absence of peroxide. Without peroxide, background levels are approximately a factor of 100 lower

than they are with peroxide. This results in low detection limits even though the efficiency of the catalysts listed in Table II is not as great as the efficiency of the catalysis in Table I.

The only catalysts to be studied in detail thus far are Cr(III), Fe(II), and I_2. The rest have only been surveyed, so the data given in Tables I and II are not final. In most cases, optimization of concentrations is likely to improve detection limits. In the case of Co(II) the listed detection limit of 10^{-11}M extrapolated from data at higher concentrations may be overly optimistic because of the difficulty of handling solutions at these concentrations.

TABLE II
Catalysts in the absence of peroxide

Catalyst	Approximate Detection limit (M)	Linear range (M)	Remarks
OCl^-	10^{-9}	—	requires O_2
Br_2	—	non-linear	not useful
I_2	10^{-9}	10^{-9} to 3×10^{-7}	squared and cubed response also observed
MnO_4^-	10^{-10}	10^{-10} to 10^{-7}	no O_2 necessary
Fe(II)	10^{-10}	10^{-10} to 5×10^{-7}	requires O_2
V(II)	—	—	requires O_2

Effect of pH

For most catalysts the optimum pH for chemiluminescence is around 11. Figure 1 shows chemiluminescence as a function of pH for Co(II), Cr(III), Fe(II) and MnO_4^-. The MnO_4^- data show that it is possible for a particular catalyst to have a pH behavior very different from that of the other catalysts.

Effect of peroxide (oxygen concentration)

Light emission from luminol systems involving peroxide is proportional to the peroxide concentration. This has been used to develop analytical methods for peroxide.[10] Figure 2 shows some of our results for Cr(III). Response is linear at concentrations less than 10^{-2}M H_2O_2.

In the Fe(II)-oxygen-luminol system, the sensitivity of response is independent of oxygen concentrations at low Fe(II) concentrations. The upper concentration limit of linear response to Fe(II) increased as the rate of oxygen supplied to the cell increased.[9]

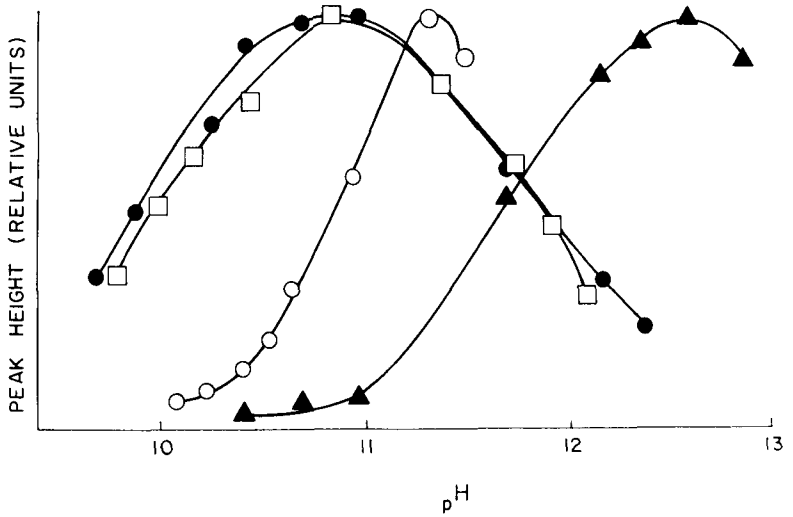

FIGURE 1 Effect of pH on chemiluminescence intensity for Fe(II) (●-●-●), MnO_4^- (▲-▲-▲), Cr(III) (□-□-□) and Co(II) (○-○-○). Relative intensities have been disregarded so four catalysts can be shown on one graph.

Conditons:

Fe(II): 2×10^{-7}M Fe(II), 10^{-3}M luminol, 80 ml O_2/min

MnO_4^-: 5×10^{-8}M MnO_4^-, 10^{-3}M luminol

Cr(III): 2×10^{-8}M Cr(III), 10^{-2}M H_2O_2 10^{-3}M luminol

Co(II): 2×10^{-8}M Co(II), 10^{-2}M H_2O_2 10^{-3}M luminol

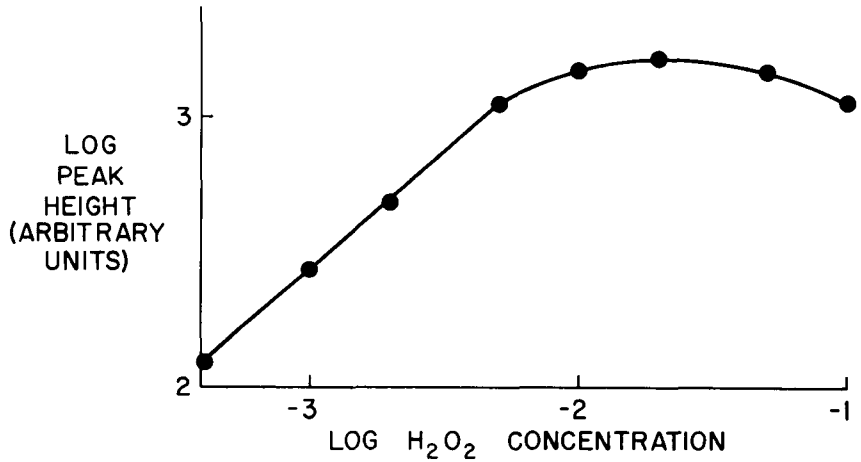

FIGURE 2 Variation in Cr(III)—catalyzed chemiluminescence intensity with H_2O_2 concentration.

Conditions:

10^{-6}M Cr(III), 10^{-2}M H_2O_2 10^{-3}M luminol, 2×10^{-2}M EDTA in sample and background, cell pH 10.3.

Effect of luminol concentration

Each catalyst has its own characteristic dependence on luminol concentration. The effect of luminol concentration on several different catalysts is shown in Figure 3. Characteristically there is a decrease in efficiency at high luminol concentrations, which may be due to luminol (or its aminophthalate oxidation product) acting as an organic complex to reduce the "availability" of the metal ions for catalysis.

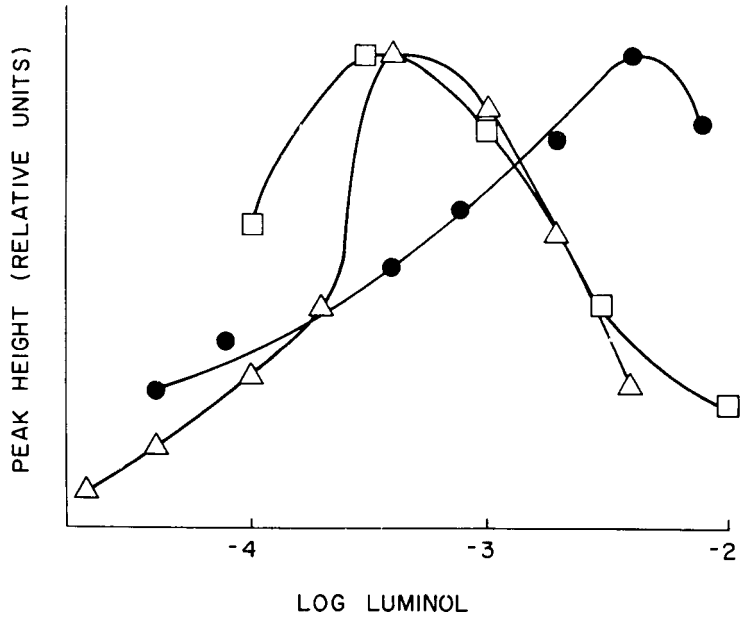

FIGURE 3 Chemiluminescence intensity versus luminol concentration for Fe(II) (●-●-●), Cr(III) (□-□-□) and MnO_4^- (△-△-△). Relative intensities have been disregarded so the data for three catalysts can be shown on one graph.
Conditions:
Fe(II): 10^{-7}M Fe(II), 80 ml O_2/min, cell pH 10.5–11.0.
Cr(III): 10^{-7}M Cr(III), 10^{-2}M H_2O_2 cell pH 10.5.
MnO_4^-: 10^{-7}M MnO_4^-, cell pH 10.5.

Effect of flow rate

Seitz *et al.*[8] have discussed the effect of flow rate. Two extremes of behavior are possible: for catalysts that react to an inert form in the cell, e.g. Fe(II) + O_2 → Fe(III), peak height is linearly proportional to flow rate; for catalysts that are unchanged in the cell, peak height is independent of flow rate. Figure 4 shows response versus flow rate for several catalysts.

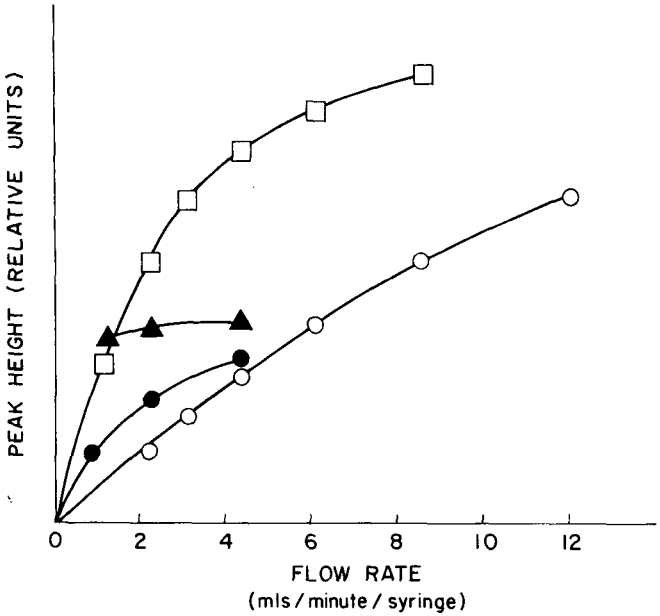

FIGURE 4 Chemiluminescence intensity versus flow rate for Ni(▲-▲-▲), Cu(●-●-●), Cr (□-□-□), and Fe(II) (○-○-○). Relative intensities have been disregarded so that all four curves can be shown on one graph.

Conditions:

Ni(II):	10^{-8}M Ni(II), 10^{-2}M H_2O_2, 10^{-3}M luminol
Cu(II):	10^{-6}M Cu(II), 10^{-2}M H_2O_2 10^{-3}M luminol, 10^{-2}M NH_3 in sample and background (No. KOH-H_3BO_3 buffer)
Cr(III):	4×10^{-7}M Cr(III), 10^{-2}M H_2O_2 10^{-3}M luminol, 2×10^{-2} MEDTA
Fe(II):	2×10^{-8}M Fe(II), 80 ml O_2/min

Effect of organic complexation

Organic complexation reduces the effectiveness of metal ion catalysis. Figure 5 shows the effect of four different complexes on Fe(II)-catalyzed light. The stronger the complex, the more effectively it reduces light. Response is still linear in the presence of organic ligands. This effect occurs for all metal ion catalysts except Mn(II), which is activated by the presence of amines, and may make it possible to determine not only the concentration of a metal ion but also its chemical form in an aqueous sample.

SPECIFIC ANALYSIS FOR CHROMIUM

Cr(III) can be determined specifically by adding EDTA to complex metal ions that would otherwise interfere.[8] The Cr(III)-EDTA complex does not

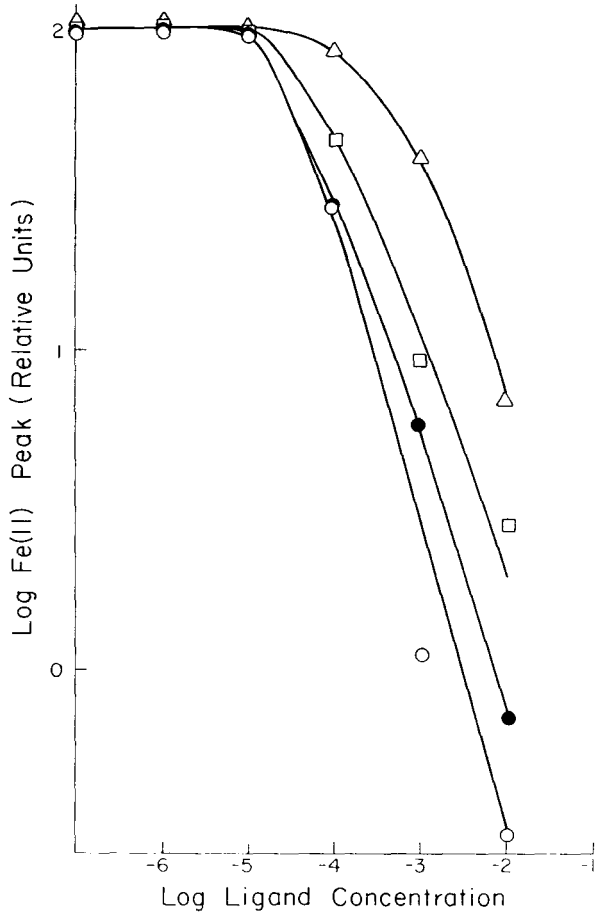

FIGURE 5 Effect of ligand concentration on Fe(II)-catalyzed chemiluminescence.

△-△-△ ethylene diamine
□-□-□ glycine
●-●-● tartrate
○-○-○ 2,4-pentanedione

Conditions:
pH 10.5–11.0, O_2 80 ml/min, 10^{-7}M Fe(II), 4×10^{-4}M luminol

catalyze chemiluminescence either, but it is kinetically slow to form.[11] The only metal ions to interfere at less than a 1000-fold excess are Co(II), Fe(II), and Fe(III). These interferences can be accounted for by running a blank. This is done by heating the sample loop of the injection valve in water at 80–90°C, followed by cooling to room temperature for 6–8 min. This treat-

ment causes all the Cr(III) in the sample loop to form the non-catalyzing Cr(III)-EDTA complex. The light emission catalyzed by Fe(II), Fe(III), and Co(II) is unchanged by heating and cooling the sample loop and may be subtracted from the total. An analysis of pond water by the method of standard additions is shown in Figure 6.

The conditions used for Cr(III) analysis were 2×10^{-2}M EDTA in the sample bottle and background, 10^{-3}M EDTA in the H_2O_2 and luminol-buffer solution to complex trace catalyst contaminants in these reagents before they enter the cell, and a pH of 4.4 in the sample bottle. The sample bottle pH is important because the rate of Cr(III)-EDTA formation increases as pH increases[11] whereas at very low pH's EDTA solubility decreases.

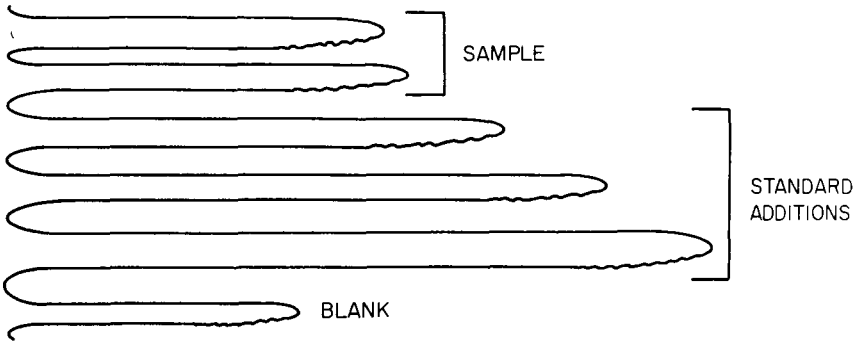

FIGURE 6 Typical recorder tracing for the analysis of Tara Pond water. Conditions:
10^{-2}M H_2O_2, 10^{-3}M luminol, 2×10^{-2}M EDTA in sample and background, cell pH 9

A detection limit of 5×10^{-10}M Cr(III) is imposed by low-level light emission from the reagents. Although the EDTA complexes trace metal impurities in the reagents to reduce background significantly, there is still light emission that may be catalyzed by Fe(III) impurities in the EDTA itself. Response is linear up to 10^{-6}M. Above 10^{-6}M, Cr(III) peaks rise to an initial spike and decay to a lower value. This is probably due to precipitation of $Cr(OH)_3$ ($K_{sp} = 10^{-30}$) in the cell after intial supersaturation.

Determination by chemiluminescence[12] of total Cr in NBS orchard leaves (Standard Reference Material 1571, which was wet-ashed with perchloric and nitric acids with a max. temperature of 265°C) gave values of 2.1, 2.1, and 2.6 mcg/g, as compared with the NBS value of 2.3. Table III shows some Cr(III) concentrations measured in natural waters.[8] The values are reproducible and in the range expected for natural waters.[13] Because chemiluminescence measures only Cr in the uncomplexed Cr(III) form, it cannot be directly compared to other methods for chromium.

The ability to distinguish different forms of chromium by chemiluminescence is of value in studying the relationship between the chemical form of chromium and its impact on the environment.

SPECIFIC ANALYSIS FOR IRON

Most of the catalysts not requiring peroxide are either strong oxidizing or reducing agents. By adding a reducing agent, such as sulfite, to destroy all the oxidants and oxidizing catalysts and to convert iron to Fe(II), chemiluminescence analysis is specific for iron.[9] Sulfite is not a sufficiently strong reductant to generate V(II) or Cr(II), the other reducing agents that catalyze luminol chemiluminescence in the absence of peroxide.

TABLE III
Chromium (III) analysis of natural water samples

Sample	Cr(III) concentration found (M)	Cr(III) concentration found Average	Equivalent Cr(III) conc. of blank (M)
Oconee River	2.5×10^{-8}		2×10^{-7}
	3×10^{-8}	3.2×10^{-8}	
	4×10^{-8}	(1.7 ppb)	
Lake Lanier	2.0×10^{-8}		
	2.2×10^{-8}	2.1×10^{-8}	4×10^{-8}
	2.0×10^{-8}	(1.1 ppb)	
Tap water	1.8×10^{-7}		
	1.9×10^{-7}	1.9×10^{-7}	3×10^{-8}
	2.0×10^{-7}	(10 ppb)	
Tara Pond	0.8×10^{-7}		
	1.0×10^{-7}	1.0×10^{-7}	2×10^{-7}
	1.1×10^{-7}	(5 ppb)	

Fe(II) is important in water where anaerobic conditions prevail. Under these conditions other species catalyzing the luminol reaction are not likely to be present. The existing colorimetric methods for Fe(II) in natural waters require chemical operations (such as acidification) that may change the ratio of Fe(II)/Fe(III) in the sample.[14-19]

The chemiluminescence detection limit for Fe(II) is 10^{-10}M; response is linear up to 5×10^{-7}M. In addition to the effect of organics discussed earlier, several metal ions—Co(II), Cr(III), Ni(II), Mn(II), and Cu(II)—interfere to reduce chemiluminescence. Figure 7 shows how they affect peak height. Co(II), Cr(III), and Ni(II) must be present in large excess to interfere.

Response in the presence of Cu(II) remains linear with concentration. Mn(II) is the most serious interference causing a curvature in calibrations. Figure 8 shows typical calibrations in the presence of interfering metals.

Table IV compares some iron concentrations measured by chemiluminescence with values obtained by other methods. The natural water samples were analyzed for total iron by the method of standard additions using

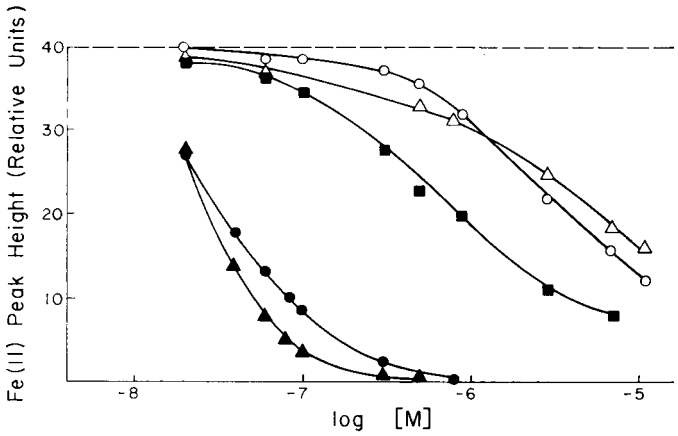

FIGURE 7 Reduction of Fe(II) peak height in the presence of varying concentrations of interfering metal ions.

O–O–O Cr(III)
■–■–■ Co(II)
△–△–△ Ni(II)
●–●–● Mn(II)
▲–▲–▲ Cu(II)
— — — Peak height in the absence of interfering metal ions.

Conditions:
O_2 80 ml/min, pH 10.5–11.0, 4×10^{-8}M Fe(II), 4×10^{-4}M luminol

sulfite as a reducing agent. To attain the optimum range for chemiluminescence analysis, they were diluted by a factor of 100 for tap water, 250 for river water and 500 for pond water.

No color developed for any of the three water samples when a conventional phenanthroline method for total iron[20] was applied to them without prior solvent extraction or ashing. This suggests that if Fe(II) were present in these samples, the colorimetric method would not specifically determine it in the presence of Fe(III), since the ashing or solvent extraction procedure would alter the Fe(II)/Fe(III) ratio in the sample.

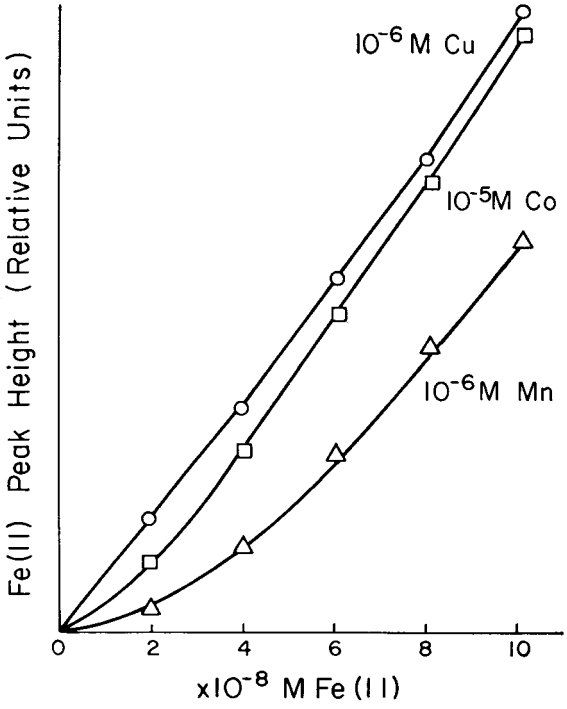

FIGURE 8 Typical chemiluminescence versues concentration curves in the presence of interfering metals.

○-○-○ 10^{-6}M Cu
□-□-□ 10^{-5}M Co
△-△-△ 10^{-6}M Mn

Conditions:

O_2 80 ml/min, pH 10.5–11.0, 4×10^{-4}M luminol

The relative magnitudes of the three calibrations have been disregarded so that all three could be shown on the same graph.

CHEMILUMINESCENCE TITRATIONS

Because some of the catalysts in Table II are common titrants, it is possible to do chemiluminescence titrations where the amount of light catalyzed by a system is measured as a function of titrant added. For example, in the titration of arsenic(III) with iodine,[21] no light will be catalyzed by the titration mixture until an excess of iodine is present. Beyond the endpoint, light intensity will be proportional to excess iodine. The endpoint can be determined by extrapolation. Figure 9 shows the data expected for a chemiluminescence titration.

TABLE IV

A comparison of iron concentrations measured by different methods in orchard leaves and water samples

Sample	Chemiluminescence analysis	Atomic absorption (mcg/ml)	Colorimetry (mcg/g)
Orchard leaves 1[a] NBS SRM 1571	240, 220 mcg/g	—	282
Orchard leaves 2[a] NBS SRM 1571	237, 251 mcg/g	—	282
Pond water	0.72, 0.83 mcg/ml	0.74	—
River water	0.39, 0.38 mcg/ml	0.34	—
Tap water	0.18, 0.15 mcg/ml	<0.30	—

[a] Orchard leaves 1 and 2 are separate ashings with nitric and perchloric acids of the same material.

The titration of arsenic is of interest because of its toxicity. Arsenic can be separated by distillation from 6M HCl as $AsCl_3$.[22] Table V shows the results of 12 chemiluminescence titrations of 2×10^{-7}M As(III) with I_2 in a 10^{-2}M phosphate buffer (pH 7), and compares them to the classical titration (to a starch endpoint) of the 0.05M stock solutions. The titrations were done by adding 50-mcl aliquots of 10^{-4}M I_2 to 500 ml of sample 2×10^{-7}M in arsenic. Three per cent more iodine was necessary to reach the chemilumi-

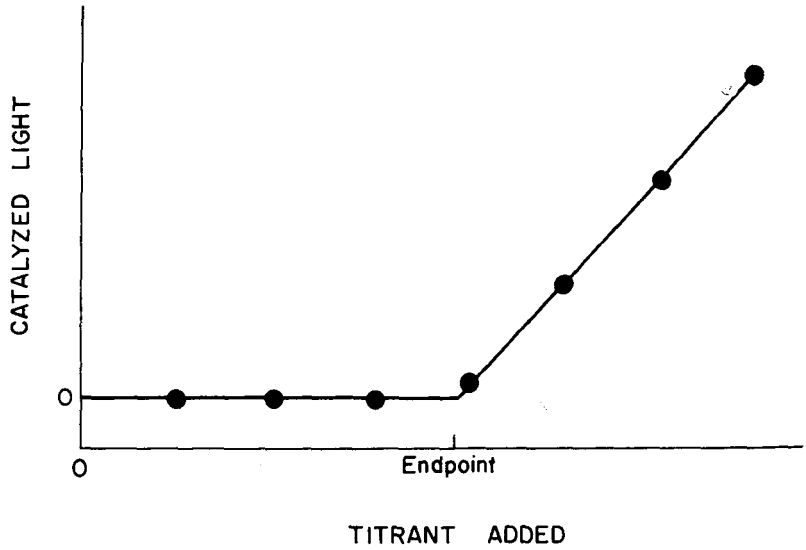

FIGURE 9 Diagram of an ideal chemiluminescence titration.

TABLE V

Chemiluminescence titration of 100.0 nanomoles As(III) with iodine

Set[a]	Titration	Nanomoles I_2 to reach endpoint	Set average
I	1	102.5	
	2	102.5	103.5
	3	105.0	
II	1	103.0	
	2	103.0	103.0
	3	103.0	
III	1	100.0	
	2	101.0	100.5
	3	100.5	
IV	1	105.5	
	2	107.0	105.0
	3	103.0	

[a] Each set represents separate 10^{-3}M As and 10^{-4}M I_2 standards prepared by dilution from 0.1M As and 0.05M I_2 standards. The 0.105M I_2 standard was standardized versus the 0.100M As (primary standard). The fact that precision within sets is greater than precision among different sets indicates that precision is lost in preparing standards by dilution.

TABLE VI

Chemiluminescence titration of 94.0 nanomoles of $SO_3^=$ with I_2

Titration	Nanomoles I_2 to endpoint
1	97.0
2	97.0
3	97.0
4	97.7
5	97.5
6	98.5
7	98.8
8	99.0
9	98.8
10	98.3
11	100.0
	Average 98.1

nescence endpoint than the classical endpoint. An actual titration is shown in Figure 10.

Iodine titration has been used to determine SO_2 in air.[23] Table VI shows the results for chemiluminescence titrations of 2×10^{-7}M $SO_3^=$ with iodine in 500 ml of 10^{-2}M phosphate buffer at pH 7.[24] A theoretical detection limit

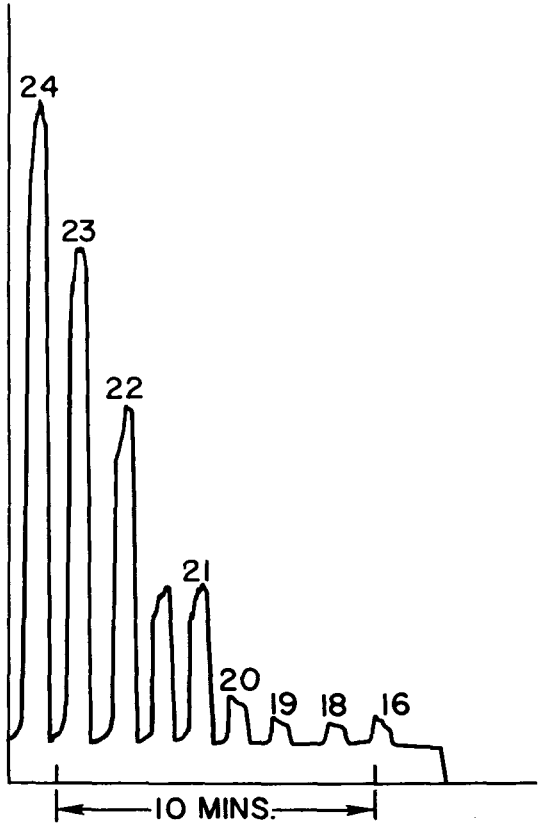

FIGURE 10 Data showing chemiluminescence titration of As(III) with I_2
The numbers over the peaks indicate how many 5-nanomole aliquots of iodine were added before running the peak.

of less than 0.01 ppm SO_2 in air was calculated, based on a one-liter air sample collected in 50 ml of solution. The time for a titration is 15–20 min.

Speed and sensitivity can be improved by observing the extent to which the SO_2 reduces the peak height from a standard iodine solution. A smaller collecting volume can be used because no volume correction is needed as in the titration.

Fe(II), V(II), MnO_4^-, and OCl^- are other possible chemiluminescence titrants.

OTHER APPLICATIONS RELATING TO THE ENVIRONMENT

Analysis for other metals using ion exchange

To determine those metals that catalyze luminol chemiluminescence but are not readily analyzed specifically, ion exchange separation is required. This can best be done by connecting the end of the ion exchange column directly to the chemiluminescence cell which serves as the detector for the column.

Anion exchange in concentrated LiCl appears to be a good medium for separation.[25] Because the luminol reaction requires bases, separations in HCl are not feasible if chemiluminescence detection is used. Nevertheless, the extensive work by Krause and associates[26-27] on separations in HCl should be applicable to LiCl. Krause *et al.*[29] did try LiCl as an eluant.

Analysis for complexing agents

Because the behavior of metal ions in water is modified by the presence of organics that form complexes, it is desirable to determine the ability of natural water to complex. The effect of complexes on metal ion catalysis of luminol chemiluminescence (see Figure 5) offers two possible approaches. If a procedure for eliminating interfering metal ions [particularly Cu(II) and Mn(II)] is developed, the intensity of catalysis by a spike of Fe(II) in a natural water sample can be compared with the intensity of catalysis by the same spike in deionized water, and the difference can be correlated with the complexing strength of the sample.

Alternatively, the complexing ability of individual organics can be determined by observing the extent to which they reduce the catalysis efficiency of metal ions. Thus, the complexing strength of an organic can be determined without actually identifying the compound. Determination of organics by measuring the extent to which they quench copper-catalyzed chemiluminescence has already been accomplished.[30,31]

Dynamics of trace metal systems

The sensitivity of chemiluminescence analysis can be used to study various aspects of trace metal systems. One example is the direct measurement of solubility products and the effect of ionic strength and complexation on them. For example, the solubilities of $Fe(OH)_2$ ($K_{sp} = 10^{-15}$) and $FeCO_3$ ($K_{sp} = 10^{-10.5}$) could be measured at the concentration levels likely to occur in natural waters.

For some metals the kinetics of conversion from one oxidation state to another can be followed by chemiluminescence. For example, the rate of oxidation of Fe(II) and Mn(II) by oxygen could be followed at concentrations typically found in natural waters rather than the considerably higher concentrations required by other methods.

FUTURE

The work described here represents less than three man-years of effort. On the basis of the accomplishments of this relatively modest effort we believe that chemiluminescence analysis should play a significant role in environmental analytical chemistry.

Acknowledgement

This work was supported in part through funds provided the University of Georgia by PHS, NIH Research Grant # GM 17913-01 from the National Institute of General Medical Sciences.

Disclaimer

Mention of trade names does not imply endorsement by the Environmental Protection Agency or the Southeast Water Laboratory.

References

1. H. O. Albrecht, *Z. Phys. Chem.* **136,** 321 (1928).
2. E. H. White, *A Symposium on Light and Life*, edited by W. D. McElroy and B. Glass (The Johns Hopkins Press, Baltimore, Md., 1961), p. 183.
3. F. McCapra, *Quart. Rev.* **20,** 485 (1966).
4. A. K. Babko and N. M. Lukovskaya, *Zh. Anal. Khim.* **17,** 50 (1962).
5. A. K. Babko and L. I. Dubovenko, *Z. Anal. Chem.* **200,** 428 (1964).
6. A. K. Babko and N. M. Lukovskaya, *Zavod. Lab.* **29,** 404 (1963).
7. A. K. Babko and I. E. Kalinichenko, *Ukr. Khim. Zh.* **31,** 1316 (1965).
8. W. R. Seitz, W. W. Suydam, and D. M. Hercules, *Anal. Chem.* **44,** 957 (1972).
9. W. R. Seitz and D. M. Hercules, *Anal. Chem.*, in press.
10. H. Ojima and R. Iwaki, *Nippon Kagaku Zasshi* **78,** 1632 (1957).
11. R. E. Hamm, *J. Amer. Chem. Soc.* **75,** 5670 (1953).
12. R. Li, unpublished results, University of Georgia.
13. W. Mertz, *Physiol. Rev.* **49,** 168 (1969).
14. G. F. Lee and W. Stumm, *J. Amer. Water Works Ass.* **59,** 897 (1960).
15. J. Shapiro, *Limnol. Oceanogr.* **11,** 293 (1966).
16. M. M. Ghosh, J. T. O'Connor, and R. S. Englebrecht, *J. Amer. Water Works Ass.* **59,** 897 (1967).
17. J. W. McMahon, *Limnol. Oceanogr.* **12,** 437 (1967).
18. J. W. McMahon, *Water Res.* **3,** 743 (1969).

19. E. T. Gjessing, *Limnol. Oceanogr.* **9,** (1964).
20. *Standard Methods,* 13th ed. (American Public Health Association, New York, 1971).
21. H. H. Willard, N. H. Furman, and C. E. Bricker, *Elements of Quantitative Analysis,* 4th ed. (D. Van Nostrand Co., Inc., Princeton, N.J., 1956), pp. 256–258.
22. D. Liederman, J. E. Bowen, and O. I. Milner, *Anal. Chem.* **30,** 1543 (1958).
23. F. P. Terraglio and R. M. Manganelli, *Anal. Chem.* **34,** 675 (1962).
24. W. Hardy, unpublished results, University of Georgia.
25. M. Neary, unpublished results, University of Georgia.
26. K. A. Krause, *Trace Analysis,* edited by J. H. Yoe and H. J. Koch (John Wiley and Sons, Inc., New York, 1957), pp. 34–101.
27. K. A. Krause and G. E. Moore, *J. Amer. Chem. Soc.* **75,** 1460 (1953)
28. G. E. Moore and K. A. Krause, *J. Amer. Chem. Soc.* **74,** 843 (1952).
29. K. A. Krause, F. Nelson, F. B. Clough, and R. C. Carlston, *J. Amer. Chem. Soc.* **77,** 1391 (1955).
30. A. A. Ponomarenko and B. I. Popov, *Zh. Anal. Khim.* **19,** 1397 (1964).
31. A. A. Ponomarenko and L. M. Amelina, *Zh. Obshch. Khim.* **35,** 2252 (1965).