STUDIES IN UNSEGMENTED CONTINUOUS-FLOW ANALYSIS

PART I. REPETITIVE DETERMINATIONS OF Cu(II) CATALYST

PART II. REPETITIVE DETERMINATIONS OF BROMINE AND CHLORINE IN GASEOUS SAMPLES AT A GAS-SOLID INTERFACE

By

SAVAKKATTUPALAYAM MUNIAPPAN RAMASAMY

Bachelor of Science
University of Madras
Madras, India
1964

Master of Science
University of Madras
Madras, India
1966

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
DOCTOR OF PHILOSOPHY
May, 1981

STUDIES IN UNSEGMENTED CONTINUOUS-FLOW ANALYSIS
PART I. REPETITIVE DETERMINATIONS OF Cu(II) CATALYST
PART II. REPETITIVE DETERMINATIONS OF BROMINE AND CHLORINE IN GASEOUS SAMPLES AT A GAS-SOLID INTERFACE

Thesis Approved:

Horacio A Mottola
Thesis Adviser

H. L. Gearhart II

K. D Berlin

George S. Dietz

Norman N Durham
Dean of the Graduate College

ACKNOWLEDGMENT

I wish to express my sincere appreciation to my adviser Dr. H. A. Mottola, for his enthusiastic guidance and helpful suggestions throughout this investigation. I am grateful to the other members of my committee, Dr. K. D. Berlin, Dr. H. L. Gearhart, and Dr. G. Dixon, for their assistance and advisement. I thank Dr. O. C. Dermer for correcting and editing the thesis manuscript.

I appreciate the financial support of the Chemistry Department of the Oklahoma State University in the form of Graduate Teaching Associateship during 1977-79 and Alumni and Friends Scholarship in summer, 1979; the National Science Foundation in the form of Graduate Research Associateship in summer, 1978 and during 1979-81.

My thanks are due to Dr. K. Ramalingam, and Dr. K. Ramarajan for all their help . I wish to thank Mr. H. Hall and Mr. W. Adkins for their help in constructing the necessary hardware and glassware. I thank all my friends in the research group, Sam, Iob, Tonia, Al, Mohmoud, Winston, Joe, Shekar, Monte, Young-Ok and Jim, for their warm friendship and providing a cheerful atmosphere in the laboratory.

I wish to express my indebtedness to my parents, thanks to my wife, children, and all my relatives. I appreciate the Management of Gobi Arts College for granting me study leave. Finally, I wish to dedicate this thesis to my sister, Sarojini, for uncle, Mr. K. S. Somasundaram, for their kindness and encouragement.

TABLE OF CONTENTS

Chapter Page

PART I. REPETITIVE DETERMINATIONS OF Cu(II) CATALYST

TABLE OF CONTENTS (Continued)

PART II. REPETITIVE DETERMINATIONS OF BROMINE AND CHLORINE IN GASEOUS SAMPLES AT A GAS-SOLID INTERFACE

TABLE OF CONTENTS (Continued)

LIST OF TABLES

Table Page

PART I. REPETITIVE DETERMINATIONS OF Cu(II) CATALYST

PART II. REPETITIVE DETERMINATIONS OF BROMINE AND CHLORINE IN GASEOUS SAMPLES AT A GAS-SOLID INTERFACE

LIST OF FIGURES

Figure Page

PART I. REPETITIVE DETERMINATIONS OF Cu(II) CATALYST

PART II. REPETITIVE DETERMINATIONS OF BROMINE AND CHLORINE IN GASEOUS SAMPLES AT A GAS-SOLID INTERFACE

Figure Page

PREFACE

Because of the difference in chemistry, instrumental setup, and procedure, the two methods of determination investigated in these studies are presented in separate parts, each complete with its own introduction, experimental apparatus and procedure, results and discussion, and bibliography.

STUDIES IN UNSEGMENTED CONTINUOUS-FLOW ANALYSIS

PART I. REPETITIVE DETERMINATIONS OF Cu(II) CATALYST

CHAPTER I

INTRODUCTION

In continuous-flow analysis the sample is introduced as a plug into a carrier stream. As it is being transported to the detection zone, a chemical reaction may take place between the analyte and the reagents in the stream, and the reaction is monitored either before or after it reaches equilibrium. In some cases, the sample is transported by the flow without any chemical reaction to the detection point. This type of analysis has brought about a renaissance in the application of wet-chemical methods to analytical methodology. The reasons for the widespread use and popularity of this kinetic-based method are its high sample throughput, ease of automation, accuracy, and reproducibility.

The credit for conception of continuous-flow analysis goes to Skeggs (1). In 1957, he suggested the use of air segmentation to prevent carryover and to preserve the identity of individual samples. The need to introduce and remove air bubbles is a disadvantage of the segmented-flow analysis, and good reproducibility and the absence of sample carryover were demonstrated to be possible in unsegmented flow streams (2). The absence of air segmentation, moreover, has been shown to provide a higher sample throughput. Both segmented- and unsegmented-flow analyses operate as open systems in which the unreacted reagents, and products are sent to waste after detection. On the other hand, the continuous, unsegmented closed-loop flow systems (3, 4) make use of a continuously circulated reservoir solution with a concurrent step for the regeneration of the main reagents. Such regeneration in the closed systems is made possible by adjusting the rates of chemical reactions in the reservoir or by maintaining the reagent at a constant concentration level through additions to the reservoir. This technique greatly minimizes the problems of increased operating cost (due to the expensive reagents) and time, encountered in the repetitive determinations but still retains all the advantages of the unsegmented open-flow systems and also minimizes wastage handling.

Kinetic methods for the determination of catalysts are of interest in trace analysis since they possess a high sensitivity, reasonable selectivity, and low limit of detection. Consequently, the incorporation of a catalytic reaction in the continuous closed-flow system should provide an analytical procedure that has the advantages of both. In the open systems, no technical difficulties can be expected for such a combination. The accumulation of injected catalyst in the closed-flow systems will result, however, in fast consumption of reservoir solution and thus render the use of such systems unsuitable. Therefore, physical removal or chemical inhibition of the catalyst after signal detection is necessary for the successful determinations of catalyst by sample injection into unsegmented closed-flow systems.

The present study illustrates the determination of copper(II) catalyst in an unsegmented, continuous, closed-flow system. The method is based on the catalytic effect of Cu(II) ions on the oxidation of thiosulfate by iron(III) in acidic medium. Electrochemical oxidation of the reaction product, iron(II), to iron(III) regenerates the monitored species (the red $[Fe(H_2O)_5SCN]^{2+}$ complex). A simultaneous electrochemical reduction of the catalyst, taking place at the cathode, permits the use of a closed-flow loop for catalyst determination. Such a method has been applied to the determination of copper in human blood serum which ranges from 0.70 to 1.40 ppm in male subjects and 0.85 to 1.55 ppm in female subjects (5).

The determination of copper in blood serum is clinically significant. A decrease in the total serum copper content is noted in cases of Wilson's disease and hypoproteinemias, while elevated copper values are associated with leukemia, cirrhosis, hemochromatosis, and various infections (6). In the absorptiometric determination of copper in blood serum, sensitive chromogenic reagents such as 1,5-diphenylcarbohydrazide, bicyclohexanone oxalyldihydrazone (cuprizone), and oxalyldihydrazide are employed but these methods need more than 1 mL of sample for determination and about 15 to 30 min for color development. Samples of smaller sizes can be analyzed with more sensitive but also more expensive techniques such as neutron activation (7), atomic absorption (8), flame emission (9), and x-ray fluorescence (10). Determinations with air-segmented continuous-flow systems using expensive chromogenic reagents are also available (11-13). Applications of catalytic methods to real samples (14-18) require small sample volumes but these procedures, being basically fixed-time, and variable-signal in nature in non-flow systems, require about 30 min per determination. The present method, although it employs the fixed-time, variable-signal procedure, being a continuous-flow approach, permits processing as many as 325 samples per hour, as a result of the optimization of experimental parameters.

CHAPTER II

GENERAL BACKGROUND

2.1 Kinetic Methods for Catalyst Determinations

The measurement of rates of catalyzed reactions for quantitative determinations of trace amounts of single species have been the most popular approach among kinetic methods of analyses. The increasing interest and use of catalytic determinations in analytical chemistry arises from the fact that they are highly sensitive and selective. The low limits of detection attainable by the use of relatively simple experimental apparatus and the availability of a large number of indicator reactions for single-species determination are also responsible for the popularity (19).

In homogeneous catalytic reactions, the rate of reaction is proportional, under certain conditions, to the concentration of the catalyst. Thus, the rate of the reaction can be used for the catalytic determination. In such reactions the catalysts are not consumed during the reaction but participate in a catalytic cycle which provides high sensitivity to the catalytic determination. Moreover, since these reactions are selective (fairly specific in enzyme-catalyzed reactions) in forming a catalyst-substrate complex, they are employed for the *in situ* determination of sought-for-species in the presence of other species which, in other methods, would interfere unless previously separated (14). The selectivity of catalytic reactions arises from the suitability of size and charge of the species involved in forming the intermediate catalyst-substrate complex. A discussion of the basic principles and methods of the catalytic determination other than with enzymes is given below. More detailed treatments can be also found (20,21).

A general mechanism for the catalytic cycle involving the formation of a catalyst-substrate complex and regeneration of the catalyst is given by

$$\begin{tikzcd}
C \arrow[r, phantom, "+"] & S \arrow[r, shift left, "k_1"] & CS \arrow[l, shift left, "k_{-1}"] & & & \text{(1)} \\
CS \arrow[r, phantom, "+"] & R \arrow[r, "k_2"] & P + Y + & C \arrow[ulll] & & \text{(2)}
\end{tikzcd}$$

where C represents the catalyst, S the substrate, CS the intermediate catalyst complex, R another reagent, and P and Y are products. The reverse of equation 2 is assumed to be negligible. The indicator reaction or the uncatalyzed reaction is $S + R \rightarrow P + Y$.

Mathematical treatment of this mechanism as a pre-equilibrium case (for which the reaction of equation 2 is rate-determining) or a steady-state case (for which the reaction corresponding to equation 1 is the rate-determining step) results in the following rate expressions, respectively:

$$\frac{-d[S]}{dt} = k_2\,[R][C]_o \tag{3}$$

$$\frac{-d[S]}{dt} = \frac{k_1 k_2\,[S]_o}{k_1([S]_o+[C]_o)+k_2[R]}\,[R][C]_o \tag{4}$$

when the rate is measured near initial reaction time or under conditions where neither side reactions nor the back reactions (of the indicator reaction) affect the rate of the catalyzed reaction, i.e., $[S] = [S]_o - [CS]$; $[C] = [C]_o - [CS]$ and $[S]_o >> [C]_o$, where the subscript "o" designates initial concentrations and others are the instantaneous ones. Under such an initial rate condition (e.g., at 1% of the overall reaction), $[R] \simeq [R]_o$. Therefore, equations 3 and 4 reduce to :

$$\frac{-d[S]}{dt} = k_c[C]_o \tag{5}$$

The above equation represents the proportionality between the concentration of catalyst and rate that is used in catalytic determinations.

In almost all catalyzed reactions, the reaction between S and R proceeds in the absence of the catalyst:

$$S + R \xrightarrow{k_3} P + Y$$

The rate of this reaction, which occurs simultaneously with the catalyzed reaction, is given by

$$\frac{-\,d[S](\text{uncat})}{dt} = k_3\,[S]_o[R] \tag{6}$$

when $[S]_o >> [R]_o$. Again, very early in the reaction, $[R] \simeq [R]_o$. Therefore,

$$\frac{-\,d[S](\text{uncat})}{dt} = k_u \tag{7}$$

Thus the total reaction rate is the sum of the rates of catalyzed and

and uncatalyzed reactions. When R is the monitored species, the rate is:

$$\frac{-\,d[R]}{dt} = k_c[C]_o + k_u \qquad (8)$$

Equation 8 forms the basis of two different kinetic techniques for determining the catalyst concentration.

2.2 Derivative Technique

The derivative technique is a straightforward approach in which the measured initial rate is related to the catalyst concentration. The measurement of the rate of the catalyzed reaction in the initial stages ensures that the entire reaction becomes zero order in all reactants and obeys equation 8, and complications resulting from the backward reaction of the products and also the side reactions are minimal. Such a measurement, however, needs a very sensitive device to monitor the small change in concentration of the monitored species in the initial stages.

2.2.(a) Direct Evaluation Procedure

Measurement of the rate of change of concentration of the monitored species, or the rate of signal change, when the measured concentration is linearly related to the signal, allows direct calculation of the catalyst concentration from equation 8. The values of k_u and k_c can be ascertained from the known concentration of the catalyst and the corresponding initial rate. A calibration plot of the initial rate against the catalyst concentration can also be used.

2.2.(b) Variable-Time Procedure

For the variable-time procedure, equation 8 can be written as

$$\frac{1}{\Delta t} = \frac{k_c[C]_o + k_u}{\Delta R} \tag{9}$$

Measurement of the Δt, necessary for a finite but short $\Delta[R]$ close to $[R]_o$, permits obtaining a working curve by plotting $1/\Delta t$ against the catalyst concentration.

2.2.(c) Fixed-Time Procedure

For the fixed-time procedure, equation 8 can be modified as

$$\Delta R = (k_c[C]_o + k_u)\ \Delta t\ . \tag{10}$$

Hence, a plot of measured ΔR at a finite but short Δt close to $t = 0$ against catalyst concentration is a calibration curve that can be used for the determination of the catalyst.

These derivative procedures, as pointed out earlier, are based on the measurement of rate under initial stages and hence require sensitive monitoring devices to detect small changes. In these cases, analysis time is relatively short, especially when a calibration plot is readily available. For noisy signals, however, these are not as reliable as the integral procedures discussed below. Except for the variable-time procedure, a linear signal response with the concentration of the monitored species is a necessary condition.

2.3 Integral Technique

The integral technique is next in choice to the derivative technique, to make use of less sensitive monitoring devices and to deal with noisy signals in the determination of the catalyst. In this technique, as in the derivative technique, the back- and side-reactions are minimized with the use of a high ratio of substrate to reagent concentration.

2.3.(a) Variable-Time Procedure

On integration of equation 8

$$\ln([R]_1/[R]_2) = (k_c[C]_o + k_u)(t_2-t_1) \qquad (11)$$

The ratio of $[R]_1/[R]_2$ is set at some constant value, and the time t_c that is required to attain the constant reagent ratio is measured. Then equation 11 becomes

$$1/t_c = (k_c[C]_o + k_u)/\ln([R]_1/[R]_2) \qquad (12)$$

So the plot of $1/t_c$ against the concentration of catalyst yields a calibration curve, useful for quantitative determination of the catalyst.

2.3.(b) Fixed-Time Procedure

From equation 11, by fixing a finite, constant time interval, t_2-t_1 (t_1 may be zero), $\ln [R]_1 / [R]_2$ becomes a function of the catalyst concentration. If $[R]_1$ is also held constant, a plot of $\log [R]_2$ against $[C]_o$ constitutes a working curve. Within limited ranges of catalyst concentration, approximate straight line plots of $[R]_2$ against $[C]_o$ can be used for catalyst determination.

Of these two, 2.2.(a) and 2.2.(b), the fixed-time procedure can be used for the determination of catalyst concentration only under pseudo-zero-order conditions (as in the initial rate measurements) so as to obtain linear calibration curves. In the variable-time procedure, the relationship between $[C]_o$ and $1/t_c$ is independent of the linearity of the instrumental response and measurements need not be made during the initial stages of the reaction.

2.3.(c) Kinetic-Plot Procedure

Another integral technique used almost exclusively by Russian chemists for determination of the catalyst is the kinetic-plot procedure. In this case, the type of kinetic-plot used depends on the reaction order on the monitored species. For first-order dependence, plots of $\ln([R]_1/[R]_2)$ against time give a set of straight lines whose slope (called pseudo-first-order rate constant, K^*) is linearly related to $[C]_o$:

$$K^* = \frac{\ln([R]_1/[R]_2)}{t_2 - t_1} = k_c[C]_o + k_u. \qquad (13)$$

As all the reaction conditions are kept constant, K^* is a function only of $[C]_o$ and therefore a plot of K^* against $[C]_o$ results in a calibration curve. In a similar procedure known as the method of tangents, the angles between the first-order plots and that for the blank are measured. A plot of tangent values of these angles against $[C]_o$ provides the working curve for the catalyst determination.

Reactions wherein an induction period exists are also used to ascertain the catalyst concentration: the induction period, t_i or its square, is inversely proportional to $[C]_o$. Working curves are obtained from the plot of $1/t_i$ or $1/t_i^2$ against $[C]_o$.

2.4 Sensitivity and Limit of Detection

The salient features that make the catalytic method of determinations comparable with other instrumental methods such as neutron activation analysis, atomic absorption, and x-ray fluorescence are its low limit of detection and high sensitivity. The limit of detection is defined here as the smallest quantity of material that can be detected with certainty. The statistical evaluation of the fluctuation in the rate of uncatalyzed reaction permits an estimation of the limit of detection, L.O.D.

$$\text{L.O.D.} = \bar{x} + 3s \qquad (14)$$

where $\bar{x}$ is the mean value of the signals corresponding to the uncatalyzed reaction (at least 30 determinations) and s is the standard deviation of the mean of these determinations. Similarly, the limit of quantitation, L.O.Q. (22), is given by

$$\text{L.O.Q.} = \bar{x} + 10s. \qquad (15)$$

The sensitivity of the method is given by the value of the slope of the working curve.

It is possible to derive appropriate theoretical expressions for the limit of detection and sensitivity from the corresponding equations for these procedures, and these are given in Table I. These expressions are helpful in designing the optimum experimental conditions to reach a lower limit of detection and higher sensitivity. For example, in the derivative procedures, a larger concentration of R provides a higher sensitivity at the cost of an increased limit of detection. Similar compromises are needed in Δt in the fixed-time (integral) and in the ratio of $[R]_1/[R]_2$ in the variable-time (integral) procedures. In all cases, however, a larger k_c and a smaller k_u are preferred since the ratio k_u/k_c is critical in determining the limits of detection (20,23).

The limit of detection, which depends on the relative rates of the catalyzed and uncatalyzed reactions and on the reproducibility in measuring the rate of uncatalyzed reaction, can be increased by choosing the reaction conditions such as temperature, so that there is a maximum difference in these rate constants and by controlling the uncatalyzed reaction, so that the standard deviations in equation 14 is minimum.

Reviews of the applications of kinetic methods of analysis are being published biennially in Analytical Chemistry, for example (19). These provide a concise account of new catalytic reactions and novel monitoring methods, and a critical evaluation of limits of detection, sensitivity, and selectivity, developed in every two-year period. Other reviews (23, 24), books (20, 25, 26), and a monograph (21) which deal with the theoretical aspects of the kinetic approach and discuss numerous examples of systems to which these techniques have been applied, are available.

TABLE I

MATHEMATICAL EXPRESSIONS FOR THE LIMIT OF DETECTION AND SENSITIVITY IN THE KINETIC PROCEDURES USED IN THE DETERMINATION OF CATALYST CONCENTRATIONS

Method	Basic Equation	Plot	Limit of detection	Sensitivity
Initial Rate (derivative)	$\frac{-d[R]}{dt} = k_u[R]_o + k_c[R]_o[C]_o$	$\frac{-d[R]}{dt}$ vs. $[C]_o$	$k_u[R]_o$	$k_c[R]_o$
Variable Time (derivative)	$\frac{1}{\Delta t} = \frac{k_u[R]_o}{\Delta R} + \frac{[K_c] R_o [C]_o}{\Delta R}$	$\frac{1}{\Delta t}$ vs. $[C]_o$	$\frac{k_u[R]_o}{\Delta R}$	$\frac{k_c[R]_o}{\Delta R}$
Fixed Time (derivative)	$\Delta R = k_u[R]_o\Delta t + k_c[R]_o[C]_o\Delta t$	ΔR vs. $[C]_o$	$k_u[R]_o\Delta t$	$k_c[R]_o\Delta t$
Variable Time (Integral)	$\frac{1}{t_c} = \frac{k_u}{(\ln[R]_1/[R]_2)} + \frac{k_c[C]_o}{\ln[R]_1/[R]_2}$	$\frac{1}{t_c}$ vs. $[C]_o$	$\frac{k_u}{(\ln[R]_1/[R]_2)}$	$\frac{k_c}{(\ln[R]_1/[R]_2)}$
Fixed Time (Integral)	$(\ln[R]_1/[R]_2) = k_u\Delta t + k_c[C]_o\Delta t$	$(\ln[R]_1/[R]_2)$ vs. $[C]_o$	$k_u\ \Delta t$	$k_c\ \Delta t$

CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Apparatus

The spectrophotometric flow system used in this study was custom-assembled and is illustrated in Figure 1. The spectrophotometric unit consisted of the following parts:

(a) A six-volt light source (MP 1021) (McKee-Pederson Instruments, Danville, CA) operated from a six-volt lead storage battery;

(b) A Jarrell-Ash, ¼ meter monochromator covering the 180 to 860 nm wavelength range, with an aperture of f/3.5;

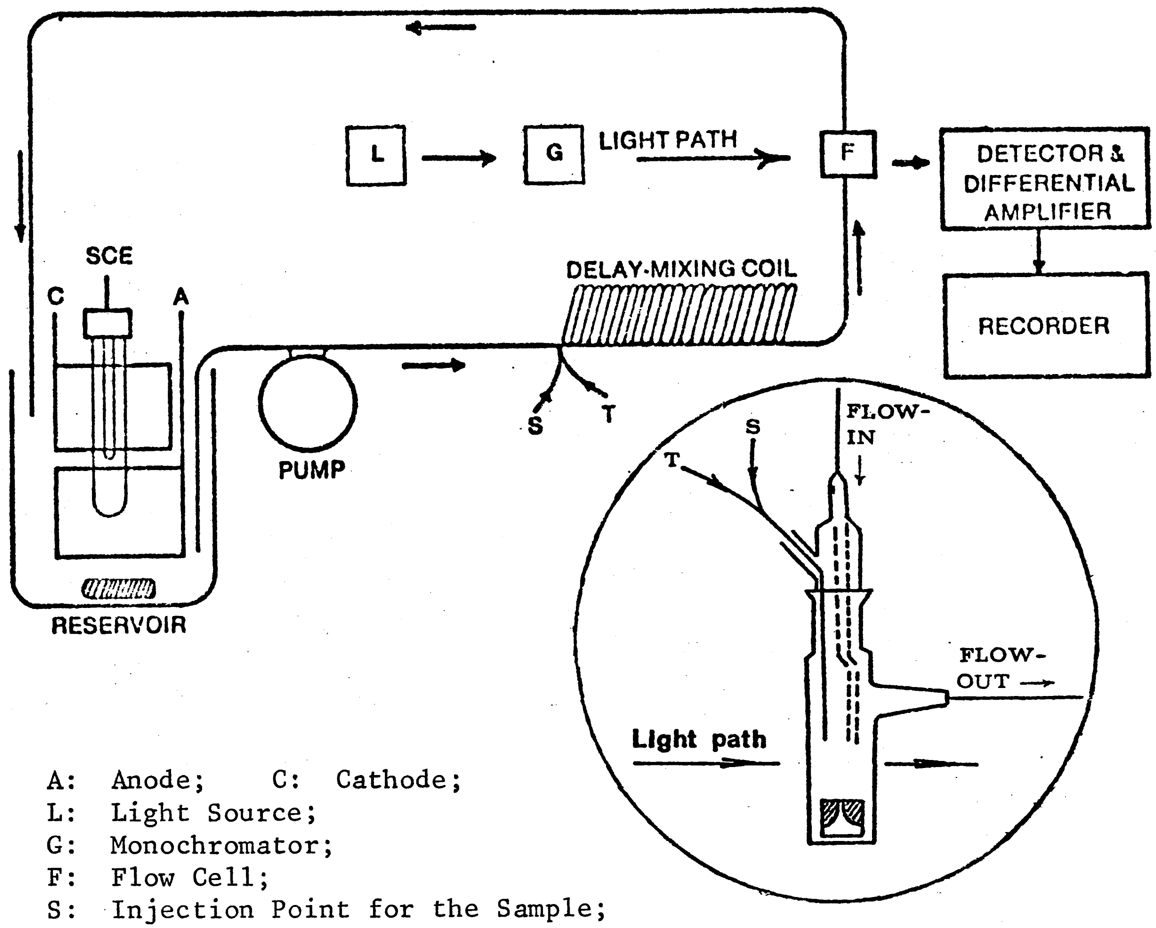
(c) A cell holder housing, designed to accommodate standard and flow-through cells, with built-in connections for temperature control of cells, magnetic stirring and external cell-flow circulation;

(d) A UDI silicone photodiode (UD 500) detector (United Detector Technology, Inc., Santa Monica, CA);

(e) A differential amplifier, Tektronix AM502 with Tektronix PS501-1 power supply (Tektronix, Inc., Beaverton, OR);

(f) A strip-chart recorder, Sargent SRL.

In studies to extract rate proportionality constants, the strip-chart readout was replaced by a Nicolet 1090A Explorer digital oscilloscope



A: Anode; C: Cathode;
L: Light Source;
G: Monochromator;
F: Flow Cell;
S: Injection Point for the Sample;
T: Injection Point for Thiosulfate;

Insert: Flow-through Cell for Direct Injection

Figure 1. Diagram of Closed-flow System for Cu(II) Determinations

with a 94A plug-in and model D amplifier (Nicolet Instrument Corp., Madison, WI).

The closed-flow system was made up of the following components:

(a) A tall beaker (500 mL) used as a reservoir of the flow solution and also as an electrolytic cell;

(b) A potentiostat-regulated power supply (MP1026) operating in the potentiostatic mode (Pacific Precision Instruments, Concord, CA) was employed for the controlled-potential electrolysis maintaining the anode potential at 0.60 V with respect to a saturated calomel electrode (SCE);

(c) Two platinum gauze cylinders were used as cathode and anode, each 3.2 cm in diameter and 3.1 cm tall;

(d) A peristaltic pump (Masterflux with SCR 7020 speed controller and 7014 pump head);

(e) A delay-mixing coil constructed with Teflon tubing of given length and 1.32 mm in inner diameter. Tubing of the same size was also used in all other parts of the closed-flow system;

(f) A flow-through cell (E-178-Q-10) of 10 mm path length with a chamber volume of 80 μL (Markson Science, Inc., Del Mar, CA).

In experiments in which injection took place directly in the detection zone, the delay-mixing coil and the above micro flow-through cell were replaced by a standard flow-through cell of 2.50 mL capacity with a path length of 10 mm, as shown as an insert in Figure 1. The reacting mixture in the standard cell was constantly stirred with a Model 19 heatless-submersible magnetic stirrer (Technilab Instruments Inc., Pequannock, NJ) and spectrophotometer cell spin-bar (Bel-Art Products, Pequannock, N. J.).

Injection of sample containing the sought-for-species and the thiosulfate reactant was accomplished by means of Hamilton gas-tight syringes and a Hamilton PB 600-1 repeating dispenser (Hamilton Co., Reno, Nev.) modified to drive two syringes simultaneously.

The reservoir solution was magnetically stirred and maintained at constant temperatures by circulating water from a Lauda/Brinkman Model K-2/R thermostat through the water jacket of the reservoir. The current during electrolysis varied from 5 to 10 mA depending on the concentration of electroactive species in the system.

3.2 Reagents and Solutions

All reagents were AR grade. The water used for solution preparation was deionized and double distilled. Typical reservoir solutions consisted of 500 mL containing 8.3×10^{-4} $\underline{M}$ Fe(III) added as nitrate, 1.6×10^{-2} $\underline{M}$ SCN^- added as the potassium salt, and 0.20 $\underline{M}$ KNO_3 and having the pH adjusted to 3.00 with $HClO_4$. Thiosulfate reagent (0.10 M) was prepared with previously boiled, cold distilled water and 3 drops of chloroform were added to improve the stability of the solution. It was stored in the dark and used within a week, during which its concentration was checked periodically by standardizing against potassium dichromate solution. A stock solution of copper(II) sulfate (1000 ppm) was prepared with acidified distilled water (pH 3-4) and diluted as required.

3.3 Procedure

The reservoir solution was subjected to controlled-potential electrolysis for about one hour, so that thermal and concentration equilibria between Fe(III) and Fe(II) were reached and as a consequence a smooth baseline without drift was obtained. Typical size of the sample injected was 20.0 µL. The simultaneously injected 0.10 M thiosulfate reagent was also of the same volume. The red complex of iron(III) and thiocyanate was monitored at 480 nm. The output voltage from the photodiode was linear with concentration (27). Since the reaction under study involves a decrease in concentration of Fe(III)-thiocyanate complex, the detector output increases. With a suitable back-up potential (~0.3 V), the signal was differentially amplified 100 times and recorded.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Kinetics of Uncatalyzed and Catalyzed Reactions

For the determination of copper(II) catalyst, using the indicator reaction involving Fe(III) and $S_2O_3^{2-}$, the overall uncatalyzed reaction can be written as:

$$2\ \mathrm{Fe(III)} + 2\ S_2O_3^{2-} \longrightarrow 2\ \mathrm{Fe(II)} + S_4O_6^{2-}. \qquad (16)$$

In spite of its wide analytical use (14, 28, 29), the mechanism of this reaction has not been well-characterized. Feigl (30) in 1957 suggested the following mechanism for the uncatalyzed reaction:

$$\mathrm{Fe(III)} + 2\ S_2O_3^{2-} \xrightarrow{\text{fast}} [\mathrm{Fe}(S_2O_3)_2]^- \qquad (17)$$

$$[\mathrm{Fe}(S_2O_3)_2]^- + \mathrm{Fe(III)} \xrightarrow{\text{slow}} 2\ \mathrm{Fe(II)} + S_4O_6^{2-} \qquad (18)$$

The catalytic activity of copper(II) was ascribed to the catalytic cycle which accelerates reaction 18 and therefore speeds up the total reaction:

$$[\mathrm{Fe}(S_2O_3)_2]^- + \mathrm{Cu(II)} \longrightarrow \mathrm{Cu(I)} + \mathrm{Fe(II)} + S_4O_6^{2-} \qquad (19)$$

$$\mathrm{Cu(I)} + \mathrm{Fe(III)} \longrightarrow \mathrm{Cu(II)} + \mathrm{Fe(II)} \qquad (20)$$

Page (31) in 1960 found no spectrophotometric evidence for the existence of the complex ion $[\mathrm{Fe}(S_2O_3)_2]^-$ and proposed that $[\mathrm{Fe}(S_2O_3)]^+$ instead was involved in the uncatalyzed reaction. His mechanism, shown below, is also based on the assumption of the existence of $(S_2O_3)^-$ and an uncharged complex, $[Fe(S_2O_3)]$.

$$Fe(III) + S_2O_3^{2-} \overset{K_1}{\rightleftharpoons} [Fe(S_2O_3)]^+ \tag{21}$$

$$[Fe(S_2O_3)]^+ + S_2O_3^{2-} \overset{K_2}{\rightleftharpoons} [Fe(S_2O_3)] + S_2O_3^- \tag{22}$$

$$[Fe(S_2O_3)]^+ + S_2O_3^- \xrightarrow[\text{slow}]{k_3} Fe(II) + S_4O_6^{2-} \tag{23}$$

$$[Fe(S_2O_3)] + Fe(II) \overset{K_4}{\rightleftharpoons} [Fe(S_2O_3)] + Fe(II) \tag{24}$$

$$Fe(II) + S_2O_3^{2-} \overset{K_5}{\rightleftharpoons} [Fe(S_2O_3)] \tag{25}$$

From a pre-equilibrium treatment of the initial stages of the reaction, it has been shown that

$$\text{rate} = k_u \cdot [Fe(S_2O_3)^+] \cdot [S_2O_3^{2-}] \tag{26}$$

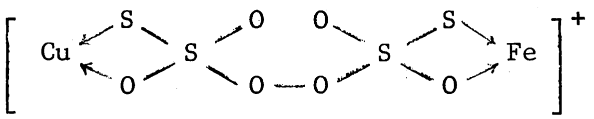
Patnaik et al. (32) reported a similar expression for the initial rate of reaction. A catalyst lowers the free energy of activation of a spontaneous reaction by following through a reaction path by which the catalyst is constantly regenerated so that the initial concentration of catalyst remains constant. In accordance with the mechanism proposed by Page (31), the following mechanism for the catalyzed reaction is postulated:

$$S_2O_3^{2-} + Cu(II) \rightleftharpoons [Cu(S_2O_3)] \tag{27}$$

$$[Cu(S_2O_3)] + [Fe(S_2O_3)]^+ \longrightarrow Fe(II) + Cu(I) + S_4O_6^{2-} \tag{28}$$

$$Cu(I) + Fe(III) \longrightarrow Cu(II) + Fe(II) \tag{29}$$

Copper(II) ions are known to form a series of thiosulfate complexes (33) such as $[Cu(S_2O_3)]$ and $[Cu(S_2O_3)_2]^{2-}$ (34), and therefore, reaction 27 is quite probable. It is also known (34) that $S_2O_3^{2-}$ reduces Cu(II) to Cu(I) and forms a soluble complex, $[Cu(S_2O_3)]^-$. The reaction between $[Cu(S_2O_3)]$ and $[Fe(S_2O_3)]^+$ species is accompanied by the simultaneous reduction of Fe(III) and Cu(II) to Fe(II) and Cu(I) respectively. This reaction is facilitated by the stabilization of Cu(I) by the thiosulfate ion in forming $[Cu(S_2O_3)]^-$ species which is reported to have a high formation constant (~ 2.2×10^{10}) (35). The selectivity in the catalytic action of Cu on this indicator reaction arises presumably from the formation of an intermediate between the reactants in reaction 28.



Though only speculative, this intermediate can be used to account for the products in reaction 28.

On the basis of the prequilibrium treatment, the rate of the catalyzed reaction is given by

$$\text{rate} = k_c\,[Fe(S_2O_3)^+]\,[S_2O_3^{2-}]\,[Cu(II)]_o \tag{30}$$

Therefore, the total rate is given by

$$\begin{aligned}\text{rate} &= k_u\,[Fe(S_2O_3)^+]\,[(S_2O_3)^{2-}]\\ &\quad + k_c\,[Fe(S_2O_3)^+]\,[(S_2O_3)^{2-}]\,[Cu(II)]_o\end{aligned} \tag{31}$$

In the initial stages of the reaction, the instantaneous concentrations of reactants are close to their initial values. Therefor, equation (31) becomes:

$$-\frac{d[\mathrm{Fe(III)}]}{dt} = k_u\,[\mathrm{Fe(S_2O_3)^+}]_o[(\mathrm{S_2O_3})^{2-}]_o$$

$$+\ k_c\,[\mathrm{Fe(S_2O_3)^+}]_o[(\mathrm{S_2O_3})^{2-}]_o[\mathrm{Cu(II)}]_o \qquad (32)$$

In this study, the same initial concentrations of reactants are used from run to run and the change of Fe(III) is measured at a finite but short Δt, close to $t = 0$. Thus equation 32 becomes similar to 10, which represents the relationship between the signal change and the catalyst concentration, under fixed time (derivative) procedural conditions. Therefore,

$$\Delta[\mathrm{Fe(III)}] = k_u + k_c\ [\mathrm{Cu(II)}]_o \qquad (33)$$

The decrease in [Fe(III)] is photometrically followed with a detector whose response is found to be linear with the monitored species. Hence,

$$\Delta(\mathrm{signal}) = k_u + k_c\ [\mathrm{Cu(II)}]_o \qquad (34)$$

Thus, the catalytic cycle provides an instantaneous regeneration of the catalytic species and the concentrations of the main reagents are such that the over all reaction is considered to proceed through a pseudo-zero-order process. This forms the basis of the determination of the catalyst under the fixed-time, variable-signal procedure.

4.2 Choice of Experimental Conditions

The rate constants for the uncatalyzed and catalyzed reactions, k_u and k_c, are reported (21) as $1.44 \times 10^4\ \mathrm{sec^{-1}\ M^{-1}}$ and $2.10 \times 10^9\ \mathrm{sec^{-1}\ M^{-1}}$ respectively. The large value of k_u precludes the use of the reactants, namely Fe(III) and thiosulfate, in the reservoir solution. In fact, a mixture of 8.30×10^{-4} $\underline{M}$ Fe(III) and 8.30×10^{-4} $\underline{M}$ $S_2O_3^-$ in presence of SCN^- becomes colorless within 30 min and so fast a reaction causes a continuous drift in the baseline.

In order to provide long-range baseline stability, one of the reagents, in this instance thiosulfate, is simultaneously injected with the sample, instead of being incorporated in the reservoir solution. Injection of the thiosulfate in a small volume (20 µL) and in relatively high concentration (0.10 $\underline{M}$) into the flow solution of Fe(III) creates a temporarily high concentration within the plug so that the uncatalyzed reaction takes place at a reasonably faster rate. When the plug reaches the reservoir, however, the concentration of $S_2O_3^{2-}$ decreases by about 2500 fold due to the dilution, and this keeps the uncatalyzed reaction from proceding at a noticeable rate.

The rates of uncatalyzed and catalyzed reactions are followed absorptiometrically by treating Fe(III) with a large excess of SCN^-, (1:20), so that only one of the various possible complexes of the formula $[Fe(SCN)_n(H_2O)_{6-n}]^{3-n}$, where n can be 1 through 6 (36), exists in the flow solution. It has been shown (37) that the $[Fe(H_2O)_5(SCN)]^{2+}$ species predominates below $[SCN^-] = 0.032$ M at zero ionic strength and 0.056 M at ionic strengths between 1 and 2. Under the experimental conditions used in this study, the concentrations of Fe(III) and SCN^- are such that the predominant species is the $[Fe(H_2O)_5(SCN)]^{2+}$ complex ion, and therefore it is the monitored species.

The use of more sensitive chromogenic agents such as salicylate, thiosalicylate, Eriochrome Cyanine R, and Chromazurol S (29) could improve the sensitivity of the determination due to high molar absorptivities of their Fe(III) complexes, but they cannot be used in closed-flow systems, owing to their large formation constants (38). In these complexes, the concentration of uncomplexed Fe(III) decreases and consequently the rate of reaction 16 is found to diminish considerably. The choice of SCN^- as a chromogen, in spite of a lower molar absorptivity for $[Fe(H_2O)_5(SCN)]^{2+}$ (~ 311 L/M. cm), is advantageous in two respects. The low formation constant of the ferric complex (~ 200) (38) allows a high proportion of Fe(III) ions to take part in the catalytic reaction. A much lower formation constant of the ferrous complex (~ 10) permits the existence of sufficient free Fe(II) for successful anodic oxidation of this species under controlled-potential conditions, and thus the regeneration of Fe(III) and of monitored species. A common difficulty encountered with the use of $[Fe(H_2O)_5(SCN)]^{2+}$ is the fading of the color, especially in daylight. This is attributed to the reduction of iron(III) by thiocyanate (39). In the present study, electrolytic regeneration of Fe(III) enables maintenance of a constant concentration of the monitored species. Also, the reservoir vessel was painted black to minimize photochemical degradation.

The electrochemical regeneration of the main reagent and the simultaneous removal of the catalyst were made possible, as already noted, with the use of controlled-potential electrolysis at the two electrodes. The anodic oxidation of Fe(II) to Fe(III) was performed by setting the anode potential at +0.60 V vs. SCE. At this potential a thiocyanate solution of Fe(II) was oxidized to the red-colored ferric thiocyanate complex, the absorbance of which remained constant within 15 min. Similarly the absorbance of a fresh ferric-thiocyanate solution was found to decrease as the electrolysis proceeded and became constant within the same period. This suggests that the electrolysis forces the attainment of equilibrium between the concentrations of Fe(III) and Fe(II) and any imbalance from this ratio is restored by the electrolysis. There is an uncertainty in measuring the anode potential due to the iR drop between the SCE and the anode, which makes the calculation of the above ratio in the reservoir difficult. The cathode potential is also incidentally controlled at -0.50 V vs. SCE in this set-up and this is more than recommended (-0.40 vs. SCE) for the controlled-potential reduction of Cu(II) in acid medium (40). In this study, a red deposit of Cu(0) was visible on the cathode when 20 µL of a solution containing more than 100 ppm of Cu(II) were injected. Injections of Cu(II) solutions containing below 100 ppm produced a blue film on the cathode, which on subsequent analysis showed the presence of copper. Thus, in a single, unique operation, the catalyst was removed from the system, and the main reagent in the indicator reaction was regenerated. These two electrochemical processes are slow enough to cause a drift in the baseline and a cumulative catalytic effect in a rapid repetitive determination procedure if the volume of the reservoir solution is small. But the use of 500 mL of reservoir solution overcomes these effects by reducing the concentration of the plug components when it reaches the reservoir. Electrolysis also helps in diminishing the rate of the uncatalyzed reaction since the $S_2O_3^{2-}$ was found to undergo decomposition in the electrolysis cell with the evolution of $SO_{2(g)}$. The current passed through the cell varied from 5 to 10 mA depending on the concentration of electroactive species in a given instant. The pH of the injected sample was adjusted to 2 - 4. At a pH lower than 2, distorted peaks were obtained because of the formation of colloidal sulfur and at a pH greater than 4 the catalytic action became very slow.

4.3 Direct Injection into the Detection Chamber

The direct injection of a sample into the detector chamber containing the flowing reagent mixture has been used (3, 41) in those cases wherein the chemical reaction between the sample and the flowing reagent reaches equilibrium in a time interval smaller than the response time of the instrumental set-up used in the measurement step. Such a direct injection of $S_2O_3^{=}$ and Cu(II) into the detection zone generated transient signals only when the concentration of Cu(II) injected was above 100 ppm. The flow rate used was 15 mL/min at 25°C. Obviously, the reaction is slow and so it does not proceed to any significant extent before the reaction mixture in the chamber is mechanically carried over by the imposed flow. The use of a slower flow of reagent could lower the limit of detection but it would cut down the number of determinations per unit time because of an increase in the time for the signal to return to baseline. The working curve in the range of 100 to 250 ppm of Cu(II) for the direct injection into the detector zone with a flow rate of 15 mL/min is shown in Figure 2. A spectrophotometric cell with less chamber volume than that presently used (2.5 mL) would increase the concentration of the reactants in the plug and as a result, accelerate the reaction and decrease the limit of detection.

4.4 Injection into Delay-Mixing Coil

In order to increase the extent of reaction and achieve maximum sensitivity, a delay-mixing coil (teflon tubing of desired length wound around a glass tube) was interposed between the injection point and the photometric cell. The diameter of the tubing in the delay-mixing coil is

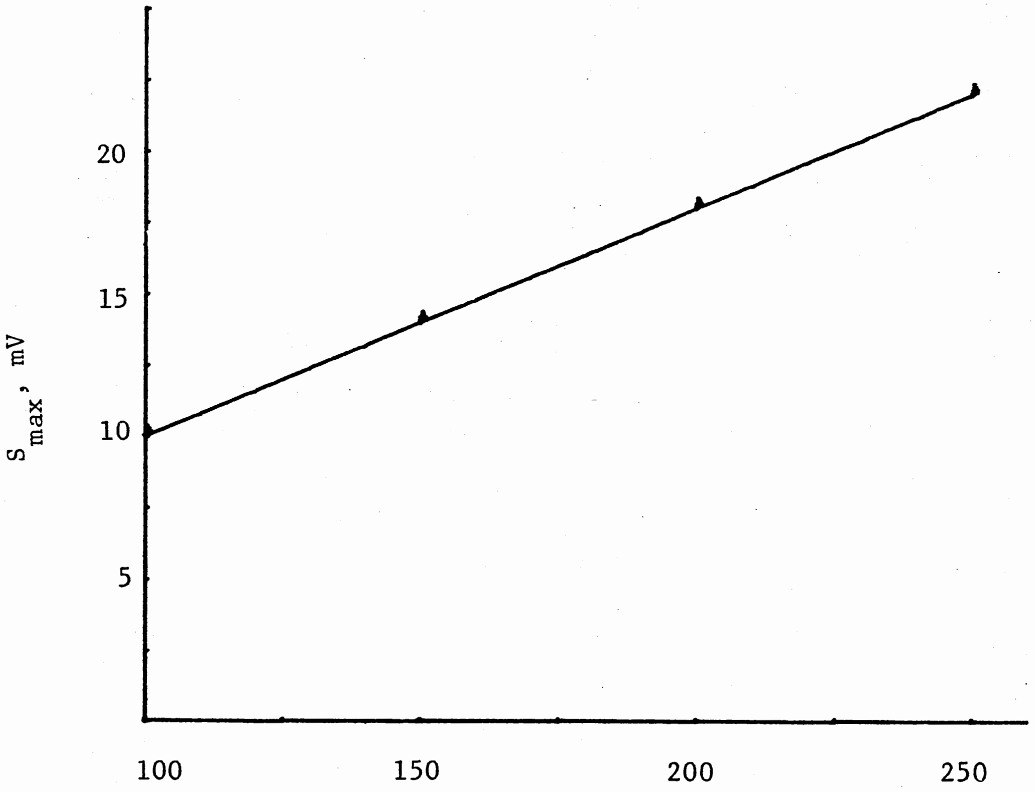


Figure 2. Working Curve for Direct Injection (S_{max} Values Given Here Are from Signals Without Amplification)

is critical because in larger tubing the mixing of the reactants in the plug would be maximum and would increase the rate of the reaction but dispersion of the plug, on the other hand, would increase the time for the signal to return to baseline, t_{bas}. Among the available tubings, one with an inner diameter of 1.32 mm was chosen for construction of the delay-mixing coil and used throughout the study. Such large tubing allows maximum mixing of the reagents and, therefore, increases the extent of the reaction. The experimental observations about the length of the coil which controls the reaction time at a given flow rate are summarized in Table II. In the selection of the optimum length of the coil, again a compromise was needed between the residence time of the plug inside the coil and the extent of dispersion. As illustrated in Table II, increase of coil length increases the signal height up to a point but also increases the time needed for return to baseline. At and above 5 meters coil length, dispersion is so large as to cancel the usefulness of the corresponding increase in the extent of reaction. A coil length of 4 meters was adopted as the one providing maximum signal height without significant change in t_{bas} when compared with shorter coils.

4.5 Effect of Flow Rate

Flow rate, by controlling the mean residence time of the plug in the delay-mixing coil, influences signal height, S_{max}, and sensitivity as well as t_{bas}. The same compromise indicated earlier for the mixing coil length is required in choosing the optimum flow rate. It has been shown (42) that the signal development with time, i.e., a transient signal as obtained in this study, can be regarded as the resultant of two first-order series processes, one describing signal growth and the other describing signal disappearance; the rate proportionality constants, k_1 and k_2, characterizing the processes of appearance and disappearance of the signal, can be extracted from the peak profile and used for method optimization. The kinetic model of the transient signal and methods of calculation of k_1 and k_2 are given in Appendix B.

TABLE II

EFFECT OF DELAY-MIXING COIL LENGTH

ON S_{max} AND t_{bas}

Coil Length (m)	Signal Sensitivity (mV/ppm)	t_{bas} (sec)
1.0	0.2	14.2
2.0	0.4	19.8
3.0	0.6	21.6
4.0	1.2	23.4
5.0	1.2	28.4

4.6 Computation of k_1 and k_2 for the Transient Signal and Optimization of Flow Rate

The procedure adopted for the extraction of the rate proportionality constants from the parameters of the transient signal can be summarized as follows: the decrease in concentration of the monitored species at peak maximum, $[C]_{max}$, is calculated using Beer's law from the value of S_{max} obtained by injecting a known concentration of Cu(II), $[B]_o$ at a given flow rate. The method I, discussed in Appendix B, was then employed to calculate the value of k_1 and k_2 at various flow rates. The maximum decrease in concentration of the monitored reactant in this case represents $[C]_{max}$ which stands for the maximum increase in concentration of the product in Appendix B. Table III summarizes the various steps in the calculative procedure. Since the value of β_{max} in this study is above 1.0, the use of method II (Appendix B) gave negative values for k_1 and k_2 and hence they are not considered.

TABLE III

CALCULATION OF RATE PROPORTIONALITY CONSTANTS
FROM THE SIGNAL PARAMETERS - METHOD I

$[B]_o$ for 5.0 ppm of Cu(II) = 7.85×10^{-6} M

Flow Rate mL/min	S_{max} (mm)	$C_{max} \cdot 10^4$ (M)	$\beta_{max} \cdot 10^{-1}$	$\kappa \cdot 10^5$	t_{max} (sec)	k_1 (sec^{-1})	$k_2 \cdot 10^5$ (sec^{-1})
4.20	102	8.67	11.00	3.05	18.89	5.50	1.68
6.82	92	7.82	9.96	3.05	10.87	9.56	2.92
9.15	83	7.06	8.99	3.05	8.03	1.29	3.95
11.92	79	6.72	8.55	3.05	6.14	1.69	5.16
14.77	80	6.80	8.66	3.05	3.76	2.76	8.44
18.11	82	6.97	8.88	3.05	2.98	3.49	10.64
21.81	94	7.99	10.01	3.05	2.50	4.16	12.70
25.44	95	8.08	10.29	3.05	2.36	4.40	13.40

The absorbance values of the flow solution as such and of its diluted solutions (1 cm path length) were measured with a Beckman 25 UV-visible spectrophotometer. The slope of the plot of the absorbance against the concentration of the iron(III) complex, from Beer's law, gives the molar absorptivity, ε of the monitored species. It was found to be 310 $L.M^{-1}.cm^{-1}$. A decrease of 0.321 absorbance units of the flow solution gave a peak height of 117 mm with 100× amplification and 100 mV span in the recorder. Therefore, $[C]_{max}$ for any other S_{max} value under the identical experimental conditions is given by:

$$[C]_{max} = A/\varepsilon b = S_{max}\ (mm)\ \frac{0.321}{117(mm)}\ /\ 310\ L.M^{-1}\ cm^{-1}.$$

$$= (8.85 \times 10^{-6}\ S_{max})\ \underline{M}.$$

The concentration of Cu(II) in the plug was calculated as follows: Injection of 20 µL of 0.01$\underline{M}$ HCl into a flow solution of 0.01$\underline{M}$ NaOH containing phenolphthalein produced a plug of volume 1.0 mL. This volume was taken as that of the plug produced when 20 µL of Cu(II) was injected into the flow solution. Therefore,

$$[B]_o = \frac{\text{ppm of Cu(II) (mg/L)}}{1000(mg/g)\ 63.54(g/M)}\ \frac{20 \times 10^{-3}(mL)}{1.0(mL)}$$

$$= (1.57 \times 10^{-6} \cdot \text{ppm of Cu(II)})\ \underline{M}.$$

The time required to reach the maximum signal value, t_{max}, was measured with a digital oscilloscope and was used in further calculations. A sample calculation of the rate proportionality constants from the signal parameters is given in Table III. The values of k_1 and k_2 calculated for the injection of 10 and 20 ppm of Cu(II) are in agreement with those obtained for 5 ppm of Cu(II). Figure 3 shows the dependence of k_1 and k_2 on flow rate; both rate proportionality constants increase with increasing flow rate in such a way that the ratio of k_1 and k_2 remains practically constant. The signal height also remains more or less constant since its value depends on the ratio of the rate proportionality constants (42). The plot of the values of S_{max} against the average flow rate, shown in Figure 4, also corroborates this trend. The increase in both constants indicates a continuous decrease in both the time to reach the peak maximum, t_{max}, and the time to return to baseline, t_{bas}. This is further supported by the experimental t_{bas} and t_{max} presented in Figure 5. The concomitant increase in k_1 and k_2 also suggests that the effect on signal parameters is mostly produced by the dynamics of flow of the plug and the rates of chemical changes have minimal impact on the values of S_{max} and t_{bas}. Because of the constancy in κ, the ratio of k_2 and k_1, over the range of flow rates studied, a rate of 20 mL/min was chosen with the instrument set-up used in this study. Higher flow rates should increase the value of S_{max} (and therefore the method sensitivity), through less dispersion and the rate of determinations per unit time, with a shorter t_{bas}. Attempts to use such a high rate showed such a trend but the results were not reproducible because of intermittent leakage of the flow solution through the connecting joints of the tubing. In spite of this, at a flow rate of 20 mL/min, as many as 325 injections per hour are possible, a rate that is higher than needed in actual situations and is competitive with that of other methods. In comparison, at 10 mL/min, the sampling rate is only 150/hour with about the same sensitivity.

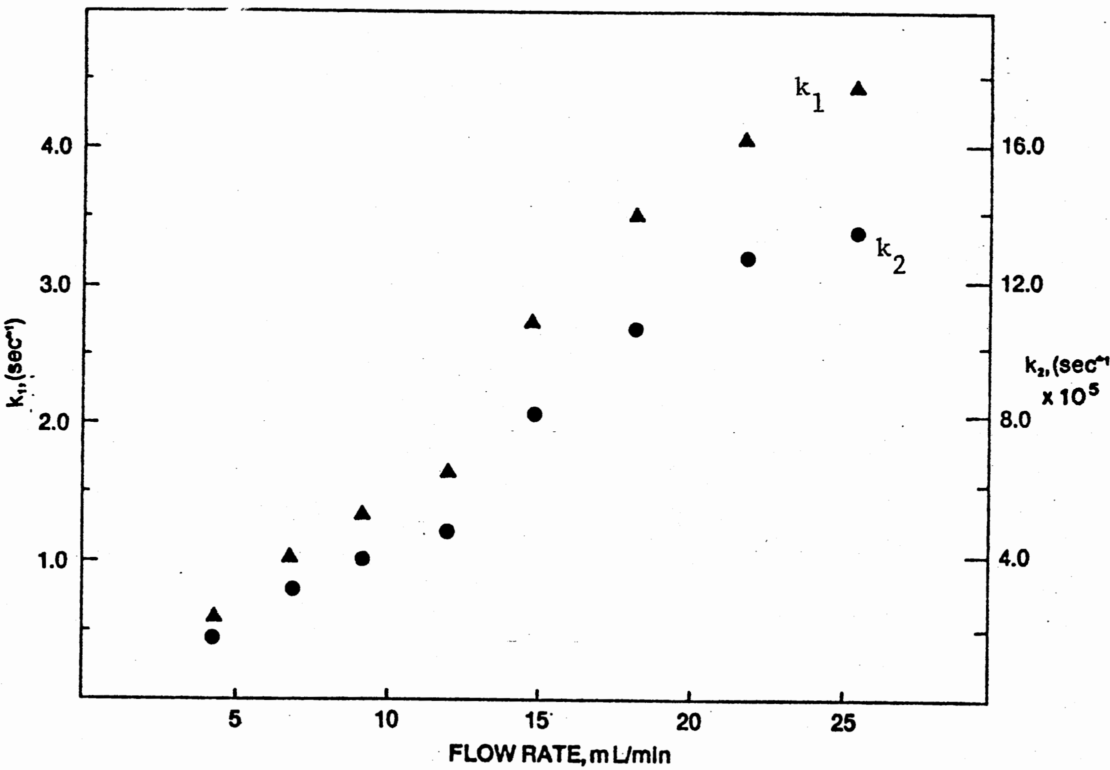


Figure 3. Variation of Rate Proportionality Constants k_1 and k_2 with Flow Rate

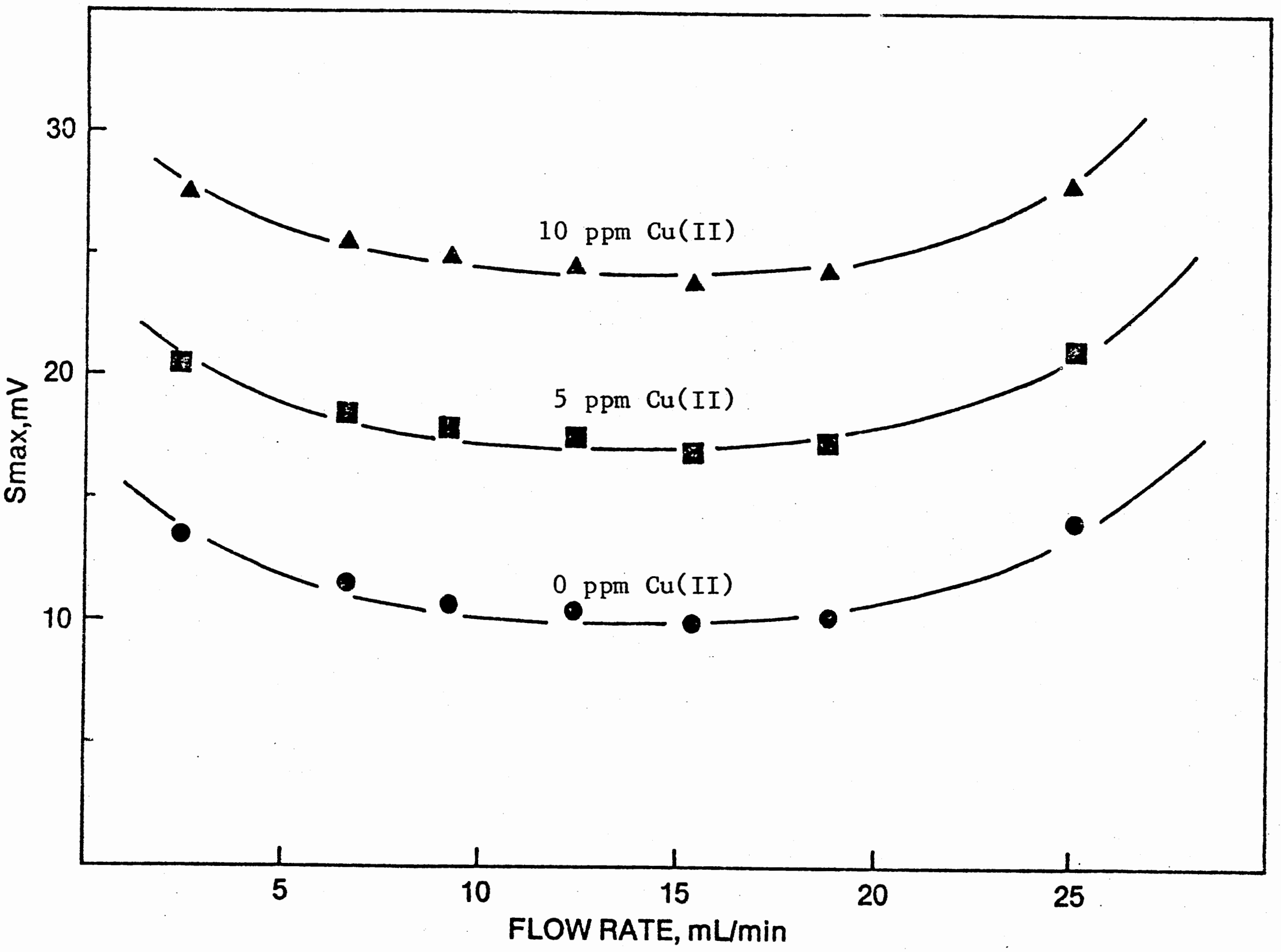


Figure 5. Variation of Signal Height, S_{max} on Flow Rate

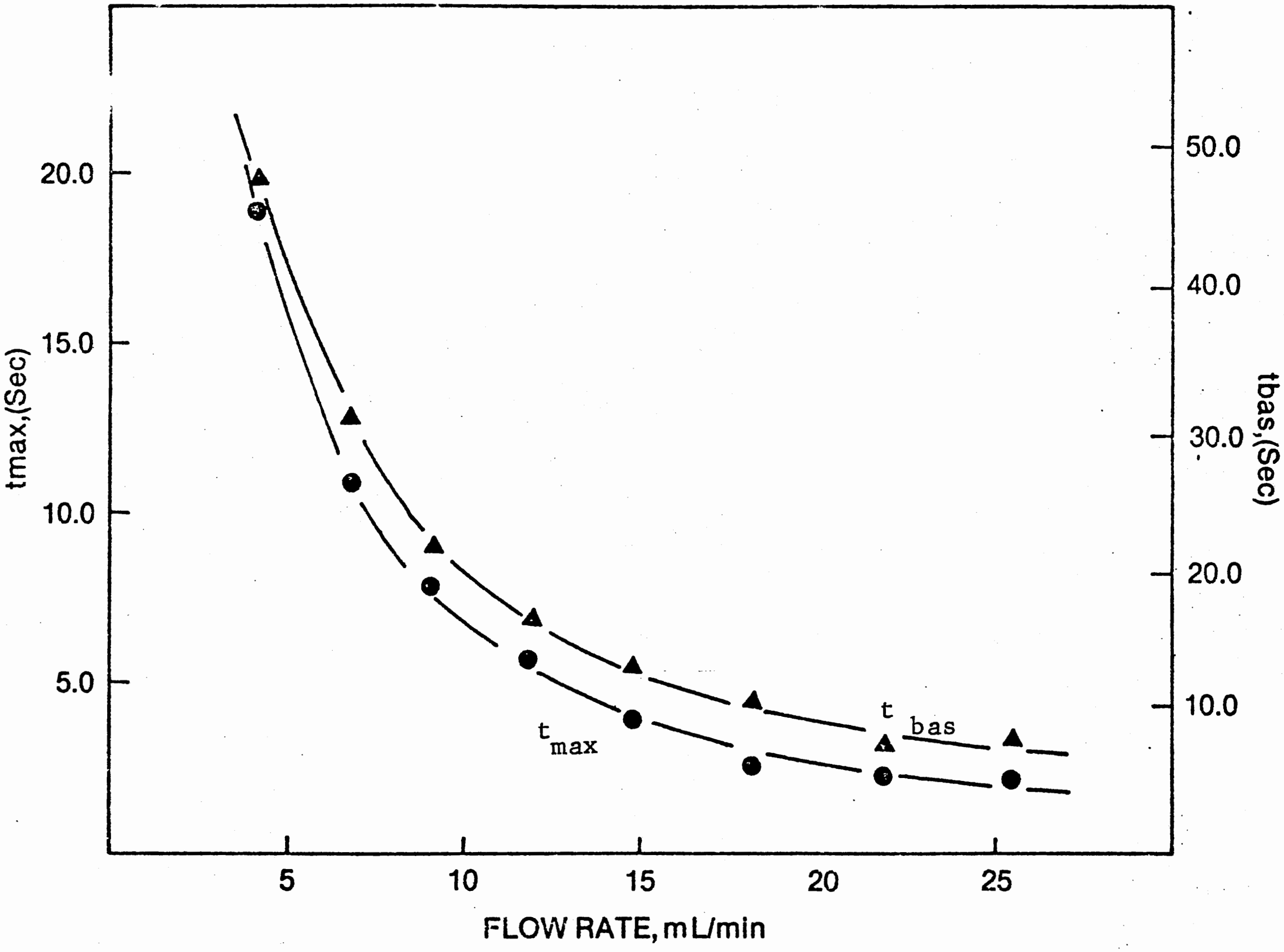


Figure 5. Effect of Flor Rate on t_{max} and t_{bas}

4.7 Effect of Temperature

The limit of detection of the method by injecting the analyte and the reagent into the flow solution at 25°C is 1.0 ppm. However, a better limit is needed in trace analysis. Khalifa et al. (14) made use of the same catalytic reaction at elevated temperature to determine sub-ppm levels of Cu(II). Therefore, the determinations were carried out with a flow solution at 40°C. Figure 6 shows typical working curves obtained at two different temperatures and with different concentrations of Cu(II) in 20.0 µL aliquots. Increase in temperature from 25°C to 40°C improved not only the method sensitivity from 1.2 to 2.8 mV/ppm but also decreased the limit of detection from 1.0 ppm to 0.25 ppm. The ratio of S_{max} (40°C) to S_{max} (25°C) for both uncatalyzed and catalyzed reactions at various concentrations of Cu(II) was found to remain constant. This indicates that the effect of temperature is mainly due to an increase in the difference of rates of uncatalyzed and catalyzed reactions. Table IV summarizes the data for direct injection and injection into the mixing coil at two different temperatures.

4.8 Determinations in Real Samples

4.8.(a) Interferences

In applying this method to determine the copper content in real samples, two types of interferences can be expected from other metal ion species: interferences with the catalytic effect of Cu(II) on the reaction and interferences with the monitoring of $[Fe(H_2O)_5(SCN)]^{2+}$. Table V gives a summary of interference studies along with some cation levels in human blood serum (average normal values). Thiourea, cysteine

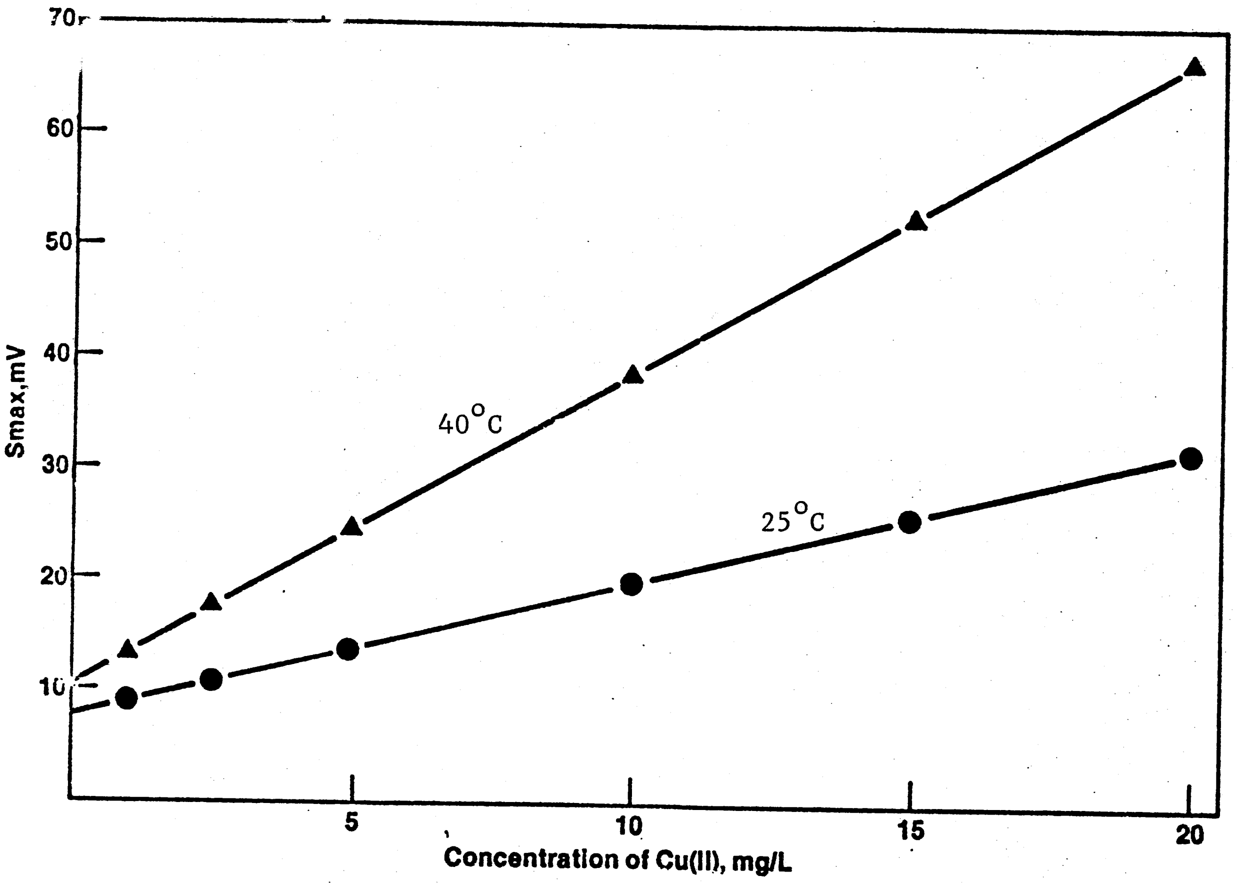


Figure 6. Working Curves for the Determination of Cu(II)

and dipyridyl ligands are capable of stabilizing Cu(I) formed in the catalytic cycle. These substances, however, when added at levels up to 10 mg/L in the reservoir solution, failed to show any activating or inhibiting effect. In higher concentrations, they complexed with Fe(III) and decolorized the reservoir solution almost immediately. A concentration of Fe(III) in the injected sample of about 25 ppm can be tolerated. Higher concentrations of Fe(III) either decreased the peak height or created a negative peak due to the formation of excess of the monitored species in the plug. Yatsimirskii (43) determined Cd(II) by using its inhibitory effect on this catalytic reaction. No such effect was observed in this study because the thiosulfate concentration was sufficiently high to cause the catalytic reaction even after complexation with Cd(II).

TABLE IV

COMPARISON OF DATA FOR DIRECT INJECTION AND INJECTION INTO THE DELAY-MIXING COIL

	Injection		
		Mixing Coil	
	Direct	25°C	40°C
Rate of determination per hour	100	150	325
	($\bar{F}$:15mL/min)	($\bar{F}$:15mL/min)	($\bar{F}$:20mL/min)
Range (ppm)	100-250	1.0-30.0	0.25-20.0
Limit of detection (ppm)[1]	100	1.0	0.25
Sensitivity (mV/ppm)[2]	0.8	1.2	2.80
Standard deviation (%) (n=30)	5.8	1.8	2.00

TABLE IV (Continued)

---

[1] Limit of detection = Average signal for the uncatalyzed reaction + 3 (standard deviation of 30 measurements of the uncatalyzed reaction)

[2] Slope of the calibration plot.

TABLE V

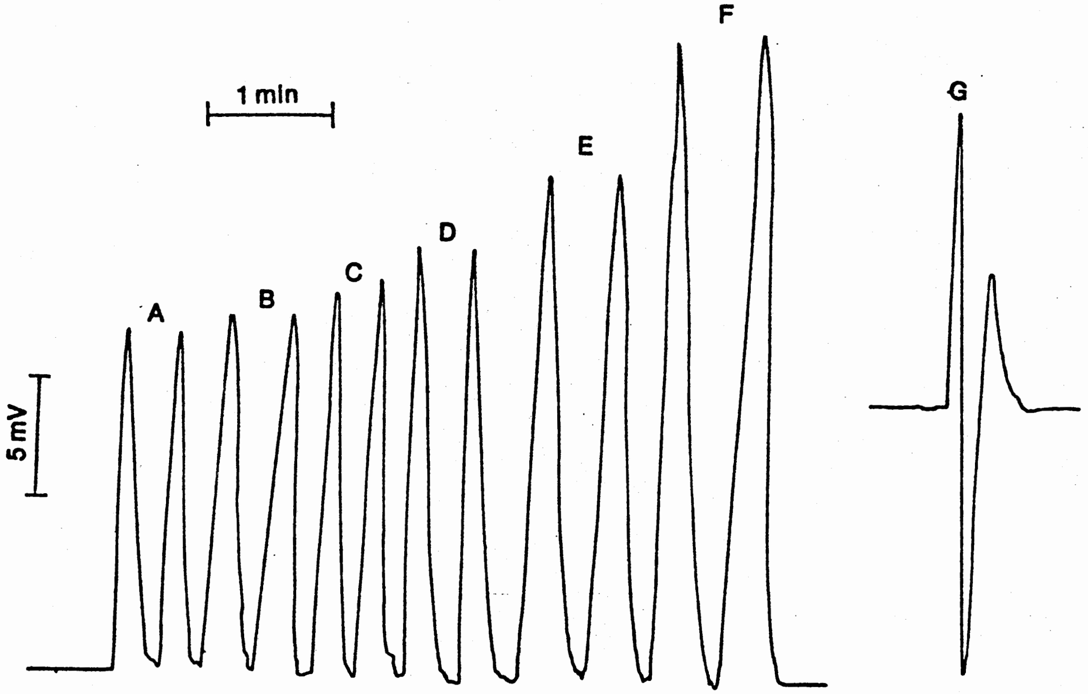
EFFECT OF SOME METALLIC SPECIES IN THE CATALYTIC DETERMINATION OF COPPER

Element	Normal Level in Serum ppm(5)	Interferent Level ppm
Na	3200	...
K	120-214	...
Ca	90-100	> 1000
Mg	36-58	> 1000
Zn	1.2	50
Cu	0.7-1.6	...
Fe(II)	0.8-1.6	100
Pb(II)	0.3-0.4	25
Al(III)	0.13-0.17	100
Cr(III)	0.03	50
Mn(II)	0.01-0.02	100
Cd(II)	0.001-0.005	50

4.8.(b) Determinations in Blood Serum

Although the metal ion concentrations of human blood serum (Table V) are much below the interferent level of this method, the direct injection of whole serum samples generated distorted peaks, probably because of complexation of either Cu(II) or Fe(III), or both, by ligands present in the proteins of the sample and also due to pH gradients. Typical signals obtained by injecting aqueous Cu(II) samples as well as the whole blood serum are illustrated in Figure 7. Deproteinized serum, however, gave well-defined and reproducible peaks. Following the procedure of Gubler et al. (44), the protein-bound copper in the serum was liberated by treatment with HCl and then the proteins were precipitated with trichloroacetic acid.

For this purpose, 0.50 mL of whole blood serum was treated with 0.25 mL of distilled water and then 0.50 mL of 2M HCl. The solution was stirred well and allowed to stand for 10 min. Then 0.50 mL of 20% trichloroacetic acid solution was added and the mixture allowed to stand another 10 min after stirring. The resulting solution was centrifuged (Clay-Adams Co. Inc., N. Y.) for 30 min. The pH of the supernatant was adjusted to 3-4 by the addition of 5M NaOH, the total volume was made to 3.0 mL with distilled water, and catalytic determination was carried out. To minimize the matrix effect in the determination of Cu(II), the method of standard additions was used. Known amounts of Cu(II) were added to the whole blood serum before treatment with HCl and proceeded as described earlier. From the values of S_{max} corresponding to the injections of the extract and the extract containing the added Cu(II) into the flow solution at 40°C, the concentration of Cu(II) in the serum was calculated.



Cu(II) in ppm: A: 0.0; B: 0.75; C: 1.5; D: 3.0; E: 5.0; F: 10.0.
Curve G: Split Peak Obtained when Whole Serum is Injected

Figure 7. Typical Signal Traces for Cu(II) Determination

Direct comparison of the results of 35 samples was made with atomic absorption measurements (6) (Perkin Elmer Model 290B). Figure 8 illustrates graphically the observed results. The Pearson correlation coefficient between results obtained by the two methods was found to be $r = 0.983$. The linear regression analysis provides a value of 1.008 ± 0.18 for the slope and 0.061 ± 0.29 for the intercept. The correlation can be considered good, the slope shows no bias toward either method of determination, and the intercept is quite below the limit of detection of this catalytic, continuous-flow method.

4.8.(c) Determinations in an EPA Water Sample

The quality-control check sample of water obtained from U.S. Environmental Protection Agency contained 37.4 ppm of Cu(II), 79.6 ppm of Fe(III), and 13 other metal ions. An aliquot of this sample, after suitable dilution and treatment with hydroxylamine hydrochloride to reduce Fe(III) to Fe(II), produced a signal corresponding to 96.3% of Cu(II). The error of 3.7% in this determination may be due to the incomplete reduction of Fe(III). A similar trend was noticed in the determination of Cu(II) in ore samples supplied by Thorn Smith Laboratories, Beulah, Michigan. The amount of reducing agent should be just sufficient to reduce Fe(III) in the samples; any excess of the reductant increases the peak height by reducing Fe(III) in the flow solution and any deficiency leaves unreacted Fe(III), which causes a negative error in the determination. This method can be applied to any sample containing less than 25 ppm of Fe(III). If a higher concentration of Fe(III) is suspected in the sample, it must be reduced. Any excess of reducing agent remaining after reduction of Fe(III) should be destroyed with bisulfite before injection into the flow solution.

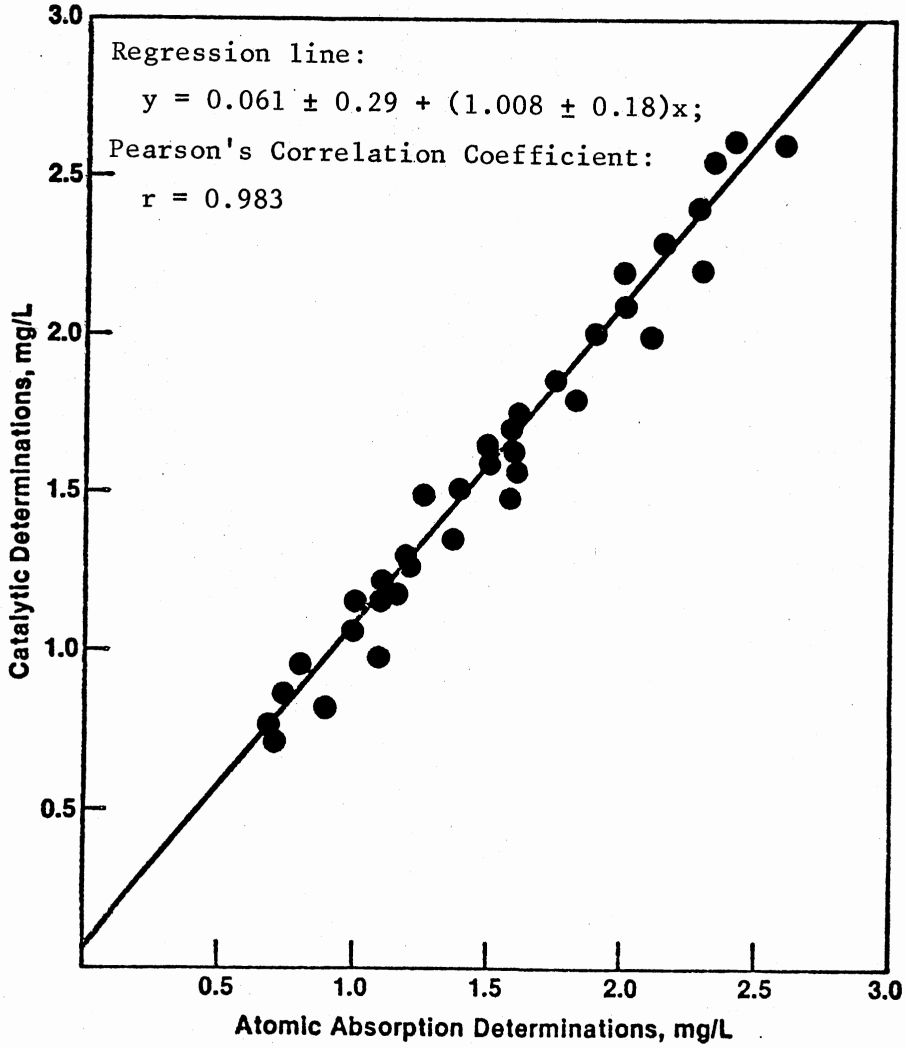


Figure 8. Comparison of Results Obtained by the Catalytic Method and Atomic Absorption Determination.

CHAPTER V

CONCLUSIONS

The study described in this part of the thesis demonstrates that a catalytic method of determination can be successfully used for trace analysis in the unsegmented, continuous, closed-flow analysis. Simultaneous regeneration of the main reagent in the flow solution and removal of the analyte after signal detection are made possible in a single electrolytic step. This makes the method sensitive, economical, and free from the problem of waste disposal. Regeneration of reagents in the closed-flow systems is possible by adjusting the rates of chemical reactions in the reservoir, by maintaining the reagent at a constant concentration level through additions to the reservoir, or by removal of the reagents through physical or chemical methods. Implementation of such techniques in the open-flow systems, wherever possible, could lead to the development of new closed-flow systems.

The method development presented in this study involved the optimization of the length of a delay-mixing coil and the flow rate towards a higher sensitivity and lower limit of detection. The instrumental set-up needed for this determination can be easily assembled and is simple; yet it affords a limit of detection and sensitivity competitive with techniques such as atomic absorption measurements. The high determination rate attained in this method is more than needed in actual analysis. The pre-treatment of real samples may be time-consuming but it is so in most methods of determination. The real advantage of this method is that it takes less than a minute to complete the determination while the equilibrium-based determinations require more than 10 min. This method, moreover, has the potential to develop into one with a completely automated procedure, so that unattended determinations are possible.

BIBLIOGRAPHY

(1) Skeggs, L. T., *Am. J. Clin. Pathol.*, 13, 451 (1957).

(2) Ruzicka, J., and Hansen, E. H., *Anal. Chim. Acta.*, 78, 17 (1975).

(3) Eswara Dutt, V. V. S., and Mottola, H. A., *Anal. Chem.*, 47, 357 (1975).

(4) Bergmeyer, H. U., and Hagen, A., *Fresenius' Z. Anal. Chem.*, 261, 333 (1972).

(5) *"The Bio-Science Laboratories Handbook"*, 10th ed.; Bio-Science Laboratories: Van Nuys, CA., 1973, p.205.

(6) *"Fundamentals of Clinical Chemistry"*, Tietz, N.W., ed., W. B. Saunders Co., Philadelphia, 1976, p. 930-932.

(7) Todd, A. P., Thorpe, M. E., and Rosenoer, V. M., *J. Clin. Pathol.* 20, 276 (1967).

(8) Berndt, H., and Jackwerth, E., *At. Absorpt. Newsl.*, 15, 109 (1976).

(9) McCullough, M. R., and Vickers, T., *Anal. Chem.*, 48, 1006 (1976).

(10) Knoth, J., Schwenke, H., Marten, R., and Glauer, J., *J. Clin. Chem. Clin. Biochem.*, 15, 557 (1977).

(11) Hirsch, H., Schenkel, H., Unger, I., and Picnic, D., *J. Clin. Chem. Clin. Biochem.*, 11, 465 (1973).

(12) Barnett, M. D., and Brozovic, B., *Clin. Chem. Acta*, 58, 295 (1975).

(13) Ijpma, S. T., Jongkind, C. J., and Liejnse, B., *J. Clin. Chem. Clin. Biochem.*, 17, 331 (1979).

(14) Khalifa, K., Doss, H., and Awadallah, R., *Analyst (London)*, 95, 207 (1970).

(15) Orlova, M. N., *Vop. Med. Khim.*, 18, 16 (1972); *Chem. Abstr.*, 76 (1972), 12388x.

(16) Alexiev, A. A., Bontchev, P. R., and Bardarov, V., *Mikrochim. Acta*, 1976 (II), 535.

(17) Otto, M., Mueller, H., and Werner, G., *Talanta*, 26, 781 (1979).

(18) Fragale, C., Bruno, P., and Fragale, G., Lab (Milan), 4, 367 (1977).

(19) Mottola, H. A., and Mark, H. B.,Jr., Anal. Chem., 52, 31R (1980).

(20) Mark, H. B., Jr., and Rechnitz, G. A., "Kinetics in Analytical Chemistry", Interscience Publishers, Philadelphia, 1968.

(21) Yatsimirskii, K. B., "Kinetic Methods of Analysis", Pergamon, Oxford, 1966.

(22) ACS Committee on Environmental Improvement, Anal. Chem., 52, 2242, (1980)

(23) Mottola, H. A., CRC Crit. Rev. Anal. Chem., 4, 229 (1975). 5

(24) Otto, M., Mueller, H., and Werner, G., Talanta, 25, 123 (1978).

(25) Mark, H. B., Jr., "Instrumental Analysis", in Bauer, H. H., Christian, G. D., O'Reilly, J. E., Eds., Allyn and Bacon, Boston, 1978, p. 523-558.

(26) Yatsimirskii, K. B., in "MTP International Review of Science: Physical Chemistry, Series one, Part 12", West, T. S., Ed., Butterworths, Oxford, 1973, Ch. 6.

(27) Chlapowski, E. W., and Mottola, H. A., Anal. Chim. Acta, 76, 319 (1975).

(28) Weisz, H., and Ludwig, H., Anal. Chim. Acta, 55, 303 (1971).

(29) Bognar, J., and Jellinek, O., Anal. Chim. Acta, 29, 395 (1963).

(30) Feigl, F., "Spot Tests", Vol. I, Elsevier Publishers, Amsterdam, 1954, p. 76.

(31) Page, F. M., Trans. Faraday Soc., 56, 398 (1960).

(32) Patnaik, D., Nanda, C., and Bakshi, K., Indian J. Chem. Soc., 34, 643 (1957).

(33) Sneed, M. C., Maynard, J. L., and Brasted, R. C., "Comprehensive Inorganic Chemistry", Vol. 2, D. Van Nostrand Co., Inc., N. Y., 1954, p. 105.

(34) Wood, C. W., and Holiday, A. K., "Inorganic Chemistry", Butterworths, London, 1960, p. 239.

(35) Brasted, R. C., "Comprehensice Inorganic Chemistry", Vol. 8, D. Van Nostrand Co. Inc., N. Y., 1961, p. 162.

(36) Sandel, E. B., "Colorimetric Determination of Traces of Metals", 3rd Edn., Interscience, 1959, Ch. 22.

(37) Eswara Dutt, V. V. S., and Mottola, H. A., Anal Chim. Acta, 94, 289 (1977).

(38) Ringbom, A., "Complexation in Analytical Chemistry", Wiley-Interscience, N. Y., 1963.

(39) Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., "Quantitative Chemical Analysis", Macmillon Co., London, 1969, p. 1049.

(40) Rechnitz, G. A., "Controlled-Potential Electrolysis", Macmillon Co., N. Y., 1963, p. 48.

(41) Eswara Dutt, V. V. S., Hanna, A. E., and Mottola, H. A., Anal. Chem., 48, 1207 (1976).

(42) Mottola, H. A., and Hanna, A., Anal. Chim. Acta, 100, 167 (1978).

(43) Yatsimirskii, K. B., Zh. Anal. Khim., 10, 339 (1955); Chem. Abstr., 50 (1956), 7647.

(44) Gubler, C. J., Lakey, M. E., Ashenbrucker, H., Cartwright, G. E., and Wintrobe, M. M., J. Biol. Chem., 196, 209 (1952).

STUDIES IN UNSEGMENTED CONTINUOUS-FLOW ANALYSIS

PART II. REPETITIVE DETERMINATIONS OF BROMINE AND CHLORINE IN GASEOUS SAMPLES AT A GAS-SOLID INTERFACE

CHAPTER I

INTRODUCTION

Unsegmented continuous-flow analysis, also known as flow injection analysis (1), is increasingly employed in clinical, industrial quality control, and pollution studies where a large number of samples of similar nature have to be analyzed for a single species. It is used largely because of less cost per analysis, shorter analysis time, simpler manifolds as compared to those for segmented continuous-flow analysis (2) and capability to process many samples with acceptable precision and accuracy by statistical treatment of data (3). Procedures employed in this technique have the common feature of introducing the analyte by means of either injection or intercalation into a continuously flowing, unsegmented stream of aqueous solution. While the sample reacts with the reagents in the flow solution, the carrier stream transports the sample to the detection area. In most cases, the analytical signal is acquired before the reaction (between the sample and the reagents) reaches equilibrium. Therefore this analytical technique belongs to the category of kinetic-based determinations.

The method presented in this study possesses all these characteristics with the unique feature that both sample and carrier stream are gases. The sample intercalated into the carrier stream is transported onto a solid mixture of a chromogenic reagent and a reducing agent. The analyte participates with the reagent in a very rapid adsorption process. As a result, the concentration of the monitored species is quickly increased. A simultaneous but slower reaction involving the reducing agent and the monitored species regenerates the reagent to its original concentration. The course of these two consecutive reactions provides a transient signal whose height is directly proportional to the concentration of the analyte in the sample. The evaluation of kinetic parameters of the signal profile are exploited for method development and optimization. The present study demonstrates the application of transient signals generated at a mixture of α-naphthoflavone and arsenic(III) on filter paper to the repetitive determinations of bromine and chlorine gases in air.

Solid reagents deposited or immobilized on solid supports have been used for kinetic and equilibrium-based determinations of analytes in aqueous samples (4). This method demonstrates a novel kinetic determination at a solid-gas interface and is the first of its kind in flow-injection analysis.

Chlorine and bromine, as they occur as gaseous contaminants in air, are commonly determined spectrophotometrically after trapping them in appropriate aqueous absorbents (5). The present method requires no such aqueous absorbents since the gaseous sample, as such, is used in the determination. Consequently, errors due to the inefficiency of the absorbent in retaining the sample, evaporation of the absorbent, and instability of analyte in the trapping solution are overcome. The method retains the simplicity of spectrophotometric monitoring and offers competitive limits of detection and sensitivity, high determination rate, good reproducibility, and accuracy. Though this method is meant for the determination of halogens in discrete samples, it can be easily adapted for continuous monitoring by appending a suitable sampling device.

CHAPTER II

A LITERATURE REVIEW OF ANALYTICAL METHODS FOR THE DETERMINATION OF HALOGENS IN GASEOUS SAMPLES

Halogens (fluorine, chlorine, bromine, and iodine) are used in halogenation processes in chemical industries, in fuel cells and propellent systems (fluorine), in water treatment plants (chlorine), and they are produced as byproducts in many industrial plants. Elemental halogens in gaseous samples are potential air pollutants causing serious health hazards. They are deleterious to many devices manufactured in the electrical and electronic industries and they damage vegetation. Radioactive iodine ^{127}I, produced up to an extent of 1% in spent nuclear reactor fuels and in nuclear explosions, is readily volatile in elemental form. Since it has a long half life (1.7×10^7 years) and concentrates in the thyroid glands (causing more harm to children than adults), iodine can be a serious air pollutant. Therefore the determination of halogens in gaseous samples is of importance in air pollution control as well as quality control in industries. Moreover, a continuous determination of unused fluorine, especially in some fluorination processes, is used to ascertain the extent of reaction. As a result, a large number of methods are being employed for this purpose. A comparison of such methods, which have been used in the determination of halogens in gaseous samples, is therefore of interest.

In this review, nine methods of determination of halogens in gaseous samples, published during the past eighteen years, are compared. Papers that are not included in this review are given in Appendix A.

The methods reviewed are: UV and visible absorptiometry, emission spectroscopy, Raman spectroscopy, x-ray fluorescence, radiochemistry, gas chromatography, thermal conductivity, electrochemistry, and titrimetry.

2.1 UV and Visible Absorptiometric Determinations

2.1.(a) Spectrophotometric Determinations

Colorimetric determinations are widely used in determining traces of the halogens because they employ well-characterized procedures, are sensitive, and utilize comparatively inexpensive instruments. The determination is based on absorption of the halogen in a liquid reagent with subsequent formation of a colored reaction product. Absorbance of the reaction product is used to estimate the concentration of the halogen from a calibration plot. The various methods differ mostly in the reagents and in the scrubbers where the gas reacts with the absorbent to form the measurable reaction product. They suffer, however, from problems of interferences, reagent stability, efficiency of the scrubber to trap the halogen, and an inherent delay in development of color when the halogen is mixed with the reagent (6).

Commonly used absorbers of gaseous samples are continuous bubblers, countercurrent flow columns, co-current flow columns, and spray chambers. Characteristics of these absorbers are listed in Table I.

TABLE I

ABSORBERS FOR AIR SAMPLING

Type of Absorber	Absorbent Capacity (mL)	Sampling Rate (Litres/min)	Remarks
Simple Bubbler	10-100	1-30	General purpose; short contact between gas and liquid
Standard Impinger	50-100	28 or less	Useful for readily soluble gases and vapors
Midget Impinger	10- 25	2.8	Useful for readily soluble gases and vapors
Scrubber with fritted-glass or other diffuser	25-100	0.5-20	Good gas-liquid contact, but diffuser has a tendency to plug
Spiral Scrubber	10-100	0.04-0.5	Effective only at low flow rates
Packed Tower	5- 50	0.5-2.0	Variable resistance; efficient only at low flow rates
Spray absorber	50-100	1-30	Capacity of absorbent depends on design and size of absorber; useful for large-volume sampling
Countercurrent Gas-Liquid Flow Contact	2.5-4	5-20	High gas flow, low liquid flow

2.1.(a).1 Determination of Fluorine

All the available colorimetric methods for the determination of fluorine are indirect; a colored compound is formed by an appropriate reagent and a cation which can be complexed by fluoride ion. Addition of fluoride ions to the solution causes the partial destruction of the colored compound and consequently an attenuation of the color. The change in absorbance of the solution permits the amount of fluorine added to be determined. Essentially they follow a general reaction pattern:

$$MR + F^- = MF + R^-$$

Table II illustrates the nature of species.

TABLE II

NATURE OF SPECIES IN THE DETERMINATION OF FLUORINE

Method	MR	MF	R
1. Zirconium-Eriochrome Cyanine R	ZrO(EcR) (red)	$ZrOF_2$ (colorless)	EcR
2. Lanthanum-alizarin complexan	$La(H_2O)_2AL$ (red)	$La(H_2O)(F)AL$ (blue)	H_3O^+
3. Thorium-thorin	$Th(TH)_2$ (violet)	ThF_4 (colorless)	TH (orange)
4. Titanium-chromotropic acid	$Ti(CTA)_4$ (red)	TiF_4 (colorless)	CTA (yellow)

<u>2.1.(a).1.1 Zirconium-Eriochrome Cyanine R</u>. This reagent has been selected as the one most suited for the colorimetric determination of fluoride ion. This choice is based on the following advantages:

it is very sensitive to small fluoride concentration differences in the range of 0.05 to 1.2 ppm. The color formation is immediate and does not require any time interval before measurement. The reagent is stable over a long period of time.

Zirconyl ion forms both mononuclear and dinuclear colored complexes with Eriochrome R in acid solution. The complexes have identical absorption spectra. When a limited quantity of fluoride is added, the zirconyl ion reacts preferentially to form $ZrOF_2$. This reaction withdraws the zirconyl ion from the colored complex and results in a decrease in the absorbance of the solution (7). Otey et at. (8) passed fluorine-air sample through a scrubber containing sodium hydroxide solution at a flow rate of 8.5 L/min. The fluoride ion content in the trapping solution was determined spectrophotometrically by this method. They were able to reach a limit of detection of 3 ppb. The precision at 95% confidence level was 5 to 15% for the fluoride levels at 650 and 50 μg respectively. The scrubbing efficiency was found to be more than 98% and was not affected by CO_2 in air. Other acidic gases like H_2S, NO_2, etc., were found to decrease the efficiency of the scrubber. Sulfate ion, if present as an impurity in the reagents or formed from atmospheric SO_3, interferes with the determination.

<u>2.1.(a).1.2 Thorium-Thorin</u>. Horton et al. (9) developed a colorimetric procedure to determine fluoride ions, based on the decrease in absorbance of a violet-colored, 1:2 complex of thorium(IV) and thorin reagent, 1-(<u>o</u>-arsenophenylazo)-2-naphthol- 3,6 -disulfonic acid, caused by the presence of the fluoride ions. The total time required for color development and decay is 15 min. Though the calibration curve does not obey Beer's law, its shape allows the determination of fluoride

in the range of 0.01 to 50 μg. The color of the reaction mixture is stable for three hours and the sensitivity is about 0.08 absorbance units/μg. Chlorine is found to interfere.

2.1.(a).2 Determination of Chlorine

2.1.(a).2.1. o-Tolidine. Chlorine in acidic solution oxidizes o-tolidine to form an intense yellow color. This well known reaction furnishes the most sensitive colorimetric method for the determination of Cl_2. Absorbance of the solution reaches a maximum almost immediately and decreases thereafter at a moderate rate (10). Nicols (11) modified a commercial SO_2 meter, for the determination of Cl_2 in air. The sample of Cl_2 is passed through a countercurrent absorption column through which is flowing an acidified o-tolidine reagent at a rate of 3 mL/min. The reaction is monitored photometrically. The limit of detection is 0.01 ppm and the sampling frequency is 20 determinations per hour. In this continuous-flow analysis, the time required for color development is kept constant by maintaining steady flow rates of the sample and the reagent. Thus the problem of a decrease in absorbance with time usually associated with this reagent is overcome. Meador et al. (12) employed a syringe sample technique to trap Cl_2 in air. A Cl_2-containing sample (47 mL), flowing in a gas line was slowly withdrawn into 3 mL of acidified o-tolidine reagent held in a disposable 50-mL polypropylene syringe and the absorbance was immediately measured. Adsorption of Cl_2 on the walls of the syringe was found to be minimum, compared to such loss in glass syringes. Moreover, reproducible results were obtained by holding the syringe perpendicular to the gas line. In this way Cl_2 was bubbled through the reagent and immediately absorbed, without appreciable loss by way of adsorption on the walls. The relative error was found to be 1.4% (38.4 ppm) to 3.4% (4.0 ppm), in the range of 0.12 to 50.0 ppm. A disadvantage of the syringe sample technique is a higher value of the limit of detection, which arises from a low ratio of gas volume to reagent volume (47:3). Ratios of 3000 and higher are commonly used in bubblers and continuous analyzers to achieve a still lower limit of detection. Bethea (13) extended the syringe technique to determine 50 to 300 ppm Cl_2, usually present in stack gas, using 3 mL of 0.1% o-tolidine. In this case, the color was stable for two hours and the relative analysis error was 3 to 5 % over the entire working range.

2.1.(a).2.2 Methyl Orange. Chlorination-oxidation of methyl orange leads to a colorless product. Consequent decrease in absorbance is the basis of the method of determination of Cl_2. Sensitivity of the method is affected by the manner in which the reagents are brought together. Slow addition of chlorine to methyl orange with vigorous stirring causes a larger decrease in absorbance than a rapid addition without stirring. This effect is probably due to a secondary reaction of the reaction product. The sensitivity of this reagent is 70% that of o-tolidine. The working range with this reagent is reported as 0.05 to 1.0 ppm (10).

A visual color comparator method to determine trace amounts of Cl_2 in aquous samples developed by Taras (14) was modofied by Thompson et al. (15) for the spectrophotometic determination of Cl_2 in air. In this method, 30 L of sample containing Cl_2 was bubbled with the aid of of fritted bubblers through an acidic solution of 3×10^{-4}% methyl orange and the absorbance of the bleached solution was then measured. The optimum Cl_2 concentration that can be determined is 0.05 to 1.0 ppm in ambient air, with an average error of less than 5%. By increasing the volume of air sampled and diluting the methyl orange solution, the limit of detection can be extended, but not by very much since about 50 L of Cl_2-free air produce the same effect as about 0.01 ppm of Cl_2 owing to the presence of trace amounts of NH_3 and other gases in Cl_2-free air. Br_2, O_3, H_2S, and NO_2 present in the sample interfere positively while SO_2 does negatively.

The American Public Health Association Intersociety Committee (16) and the National Institute for Occupational Safety and Health (17) recommended the methyl orange method for the determination of free Cl_2 content in working environments. In their technique, the Cl_2 sample is directly drawn into methyl orange solution. At a flow rate of 1 L/min, and an ambient Cl_2 concentration of 1 ppm, the maximum sampling period is limited to 30 min. If during this period there is a peak concentration of 5 ppm for 5 min, the methyl orange solution would be bleached within 10 min. Dharmarajan et al. (18) modified the above procedure, using fritted midget impingers containing sodium hydroxide solution to trap the Cl_2 sample. By adding incremental aliquots of the sample solution to the methyl orange solution, the absorbance of the final solution is controlled to the optimum range (minimum error) of the calibration plot. This procedure extends the sampling period to an 8-hour work shift.

2.1.(a).2.3 p-Nitroaniline. Another spectrophotometric method is based on the reaction between free Cl_2 and *p*-nitroaniline in alkaline solution to give a stable colored product of undetermined composition.

Gabbay et al. (19) employed a chromic acid scrubber to remove most of the interfering gases. An air sample was then bubbled through impingers containing the alkaline reagent. The sampling volume was adjusted so as to give a Cl_2 concentration of 0.2-50 ppm. After an interval of 3 min, the absorbance of the solution was measured. Samples that produced readings corresponding to the nonlinear portion of the calibration plot were diluted with the reagent. Results were reproducible within 1% and and collection efficiency of the reagent was 99%. Though this reagent is less sensitive than o-tolidine, the color developed is more stable. The chromic acid scrubber used in this technique oxidizes SO_2, NO_x, NH_3, and H_2O_2, and prevents their interference. Br_2, HCl and I_2, however, interfere in the determination.

2.1.(a).2.4 Potassium Iodide. Another frequently used method for the determination of Cl_2 and Br_2 in gaseous products of chemical reactions is to pass the gas through bubblers containing potassium iodide solution. The halogen liberates I_2 from the iodide. Most of this is fixed by the iodide in the form of triiodide but any I_2 carried out in the effluent air is trapped by a second bubbler. The solutions are mixed and the triiodide ion is colorimetrically monitored.

Noweir (20) used this method to determine Cl_2 in the decomposition products of carbon tetrachloride. Chlorine and chlorine dioxide were trapped in 30% potassium iodide buffered to pH 7 and the liberated I_2 was measured under neutral and acid conditions. One mole of Cl_2 releases one mole of I_2 under both neutral and acid conditions while one mole of chlorine dioxide releases a total of 2.5 moles of I_2, 1/5 of it under neutral conditions and 4/5 of it under acid conditions. On the basis of this stoichiometry, concentrations of Cl_2 and chlorine dioxide were determined. Low concentrations of oxidizing and reducing agents present in the sampled air did not interfere. The limit of detection for Cl_2 was 0.02 ppm with an error of 0.2 ppm.

Some of the difficulties encountered with the colorimetric determination of Cl_2 are fading of colour (o-tolidine), and relatively inconvenient procedures (methyl orange). Also, the results obtained are influenced by the rate of sampling and lack of reproducibility (methyl orange). The interference from oxidizing agents such as NO_2, H_2O_2, and O_3, and reducing agents like SO_2, H_2S, and thiols, occurs in all these methods. A comparison (20) of sensitivity, precision, range, limit of detection, selectivity, and reagent stability (21) showed that o-tolidine and methyl orange are the more suitable reagents for the colorimetric determination of Cl_2.

2.1.(a).3 Determination of Bromine

There are no colorimetric reagents for Br_2 that are specific as well as satisfactory in other respects. Some of the most sensitive reagents respond to Cl_2 as well as Br_2. Among these are methyl orange, o-tolidine, rosaniline, and the König reagent. The use of these reagents, therefore, requires a complete separation from free Cl_2. Other reagents such as Phenol red or fluorescein can be used in the presence of traces of free Cl_2. But they are less sensitive or suffer from other defects; for example, fluorescein is capable of forming eosin and other bromination products.

2.1.(b) UV Absorptiometric Determinations

2.1.(b).1 Displacement Reaction with Sodium Chloride

Weber and Howard (22) used a photometric analyzer for the continuous determination of fluorine in gas mixtures. The sample stream is passed through hot (250°C) sodium chloride where the fluorine quantitatively liberates Cl_2; this is cooled and then measured at 360 nm in a pressure-controlled flow colorimeter.

$$F_2 + 2NaCl \rightarrow 2NaF + Cl_2\,(g)$$

The analyzer consists of the hot sodium chloride reactor, a flow photometer pressure control system, a flow limiter, a vacuum pump for drawing a continuous sample through the analyzer, and a recorder. The range of the analyzer, calibrated with standard fluorine-nitrogen mixtures is 0.05 to 15 mole % of fluorine. The limit of detection is 0.05 mole % fluorine with a relative standard deviation of 1.5%. This method is free from interferences due to HF, other gases (such as Br_2, nitrogen dioxide, and UF_6) which do not absorb radiation near 360 nm and still other gases (such as O_3, ClF_3 and Br_2) which do not liberate Cl_2 from sodium chloride. One charge of 100 g NaCl in the reactor is sufficient for 30 hours of operation at an average fluorine content of 1% and a sample flow rate of 100 mL/min. With a shorter path length and/or lower pressure the range could be increased. Conversely, a longer path length and/or high pressure would provide a lower limit of detection. The absorbance of fluorine for 1-cm path length at 0°C and 760 Torr is 0.3 while that of Cl_2 is 3.0 at 330 nm. It is apparent, therefore, that a photometric filter with transmission peak at 330 would provide a higher sensitivity.

2.1.(c) Reflectance Determinations

This is based on the measurement of light reflected from a stain produced on materials impregnated with reagents for specific gases. One of the techniques of this kind uses a tape sampler which operates by passing a gaseous sample through a chemically impregnated filter tape, advanced at a constant speed from a supply reel to a take-up reel. During the sampling period, which can be varied, the tape is sealed from both sides. These tapes are examined by either light transmission or by light reflectance from the sampler. The degree of filter-staining is related to the concentration of the halogen.

Denenberg and Kriesel (23) used such a continuously moving chemically impregnated paper tape specific to Cl_2 (the name of the reagent is not disclosed by the authors). As the paper moves at a speed of 10 cm/hr past the orifice, a sample of air is aspirated through the top half of the tape at a flow rate of 500 mL/min. After exposure, the tape moves to the readout section where both halves of the tape are illuminated from a common light source through a matched fiber optics system. Two photodetectors, positioned at 45^o to the tape surface, measure the reflected light from the two tracks of the tape. The difference in the intensities of the reflected light between them, related to the Cl_2 concentration, is recorded. The output from this continuous monitor corresponds to the real time/concentration profile. This technique allows monitoring peak values in excess of the allowable limit and extended exposures above 1 ppm. Denenberg, Kriesel and Miller (24) used a similar modified, battery-operated, continuous monitoring device to determine Cl_2 in chemical industries. Gelman and Young (25) suggest monitoring Cl_2 by the use of 4,4'-bisdimethyl-aminobenzophenone, which turns from yellow to blue, and determining $Cl_2+Br_2+I_2$ with fluorescein, which undergoes a color change from yellow to red.

2.2 Emission Spectroscopic Determinations

Emission spectroscopic analysis is a method which utilizes the emission spectrum. When a sample is energized by heating or discharge, it is atomized at high temperature and then electronically excited. During the return to a stable low energy level, the sample emits characteristic radiation; the spectrum is developed on a photographic plate or measured with a photomultiplier tube. The major defects of this technique are: higher limit of detection, poor reproducibility, longer analysis time and the need for a high technical skill.

2.2.(a) Spectrographic Determinations

Grove and Loske (26) used an inert gas (He-Ar) shielded tungsten arc to detect and monitor F_2 and Cl_2 in inert gases. Known concentrations of Freon-12 and Freon-14 were used as the source of F_2-Cl_2 and F_2, respectively. Concentrations of 0.25 and 0.5% of argon were the internal standards. The basic equipment was a Jarrel-Ash spectrograph fitted with a quartz dome which served as the shield gas atmosphere chamber. Electrodes were tungsten containing thorium with cone-shaped tips. The shield gas flow rate was 10 L/min. The analytical lines selected were 6856 A^o and 7398.7 A^o (fluorine), and 8376.0 A^o (chlorine). The argon lines selected as the internal reference lines were 6965.4 A^o, 7384.0 A^o, and 8624.5 A^o. The plot of the ratio of the intensities of the halogen and argon lines against the concentration of the halogen, was linear up to 1000 ppm with a limit of detection of 20 ppm.

Burrows and Horwood (27) applied an acetylene-oxygen flame to detect airborne flurine by formation and excitation of SrF molecular ion. At a given flow rate of air sample of 100 L/min and with 5 min exposure time for the recording of spectra, the limit of detection, determined from the SrF band head/background ratio of 0.3, was 47 ppb. Air samples were mixed with a spray solution of $Sr(NO_3)_2$ produced by an atomizer. The mixture of air and solution apray was passed into the acetylene-oxygen flame. Molecular spectra of SrF were recorded on a photographic plate and the absorbances at the SrF band maxima at 5772 A^o and 5780 A^o were measured with a microphotometer.

2.3 Laser Raman Spectroscopic Determinations

A laser beam, being highly monochromatic and intense, is widely used as excitation source in Raman spectroscopy. Laane and Krishnan (28) have used an argon laser (514.5 nm, 16 W) with multipass optics and a phototube detector to determine low concentrations of chlorine in air. The sample is contained in a quartz cell of 3 cm path. The intensities of vibrational bands of chlorine in the 500-600 cm^{-1} range were monitored at 770, 180, 44, 11 and 3 Torr of chlorine in air. The plot of log P(Torr) vs. log I (intensity in counts per sec.) for the 554 cm^{-1} Raman line was linear with an intercept at a gas pressure of 0.01 Torr. This corresponds to a limit of detection of 0.3 ppm. The rotational Raman spectrum of chlorine is found to be sensitive to concentration of chlorine, but interference due to overlap of bands prohibits its use for quantitative determination.

2.4 X-ray Fluorescence Spectroscopic Determinations

X-ray fluorescence spectroscopy is the widely used x-ray technique for quantitative determination of halogens in gaseous samples. Characteristic x-rays, generated by bombarding a sample with either high-energy particles such as electrons or alpha particles or with x-ray photons, arise from the transition of an electron from a higher energy shell to a vacant inner shell of the atom of the sample. Owing to a limited number of possible inner shell transitions, the x-ray spectrum is much simpler than the optical spectrum that results from the removal or transition of valence electrons. The intensity and wavelength of x-rays are essentially independent of the chemical or physical state of the element emitting them. As a result, this technique does not distinguish the halogens from halides present in the gaseous samples. The spectrometer consists of an excitation source, a multisample chamber that can be evacuated, and a high-resolution frequency-sensitive semiconductor coupled to a multi-channel analyzer. This method, inherently very precise, rivals the accuracy of wet chemical techniques in analysis for elements with atomic number > 12. It serves as a complementary procedure to optical emission spectrography because the sample need not be an electrical conductor. It, however, suffers from matrix effects.

Lorenzen (29) used a filter cartridge made of four filters. The first filter collects particulate matter from air; the second, Whatman #41 filter paper impregnated with o-tolidine, collects Cl_2; the third, $AgNO_3$-impregnated paper, collects H_2S, and the fourth, NaOH-impregnated paper, collects SO_2 and any other remaining acidic gases. The individual filters are analyzed by x-ray fluorescence with a low power x-ray power supply (50 KV @ 5 mA), a rhodium target tube and Si(Li) detector with approximately 150 eV resolution at 5.9 KeV. The concentration of chlorine in the unknown sample is determined from a calibration plot. The detection limit for Cl_2 is 0.17 $\mu g/cm^2$. The measurable range of Cl_2 for a 96-hour air sample collected at a flow rate of 1 L/min is 0.3 to 13 ppm. Each determination takes less than 1 min per filter. The factors which affect the precision of these results are the temperature and the humidity of the sample. It was also observed that as much as 25% of the chlorine present on the filter paper disappeared within two weeks, probably due to the evaporation of HCl present along with Cl_2 in the air sample.

Tanner, Young, and Cooper (30) compared the results obtained from neutron activation analysis with those of x-ray fluorescence analysis, for the determination of Cl_2 and Br_2 along with other 33 elements present in aerosol samples. Cellulose filter papers were used to collect the samples using high-volume air pumps. Each sample was analyzed, first by the x-ray fluorescence method and then by the neutron activation technique. The concentration of the elements in the sample were determined by direct comparison of the sample x-ray counting rate with the counting rate obtained from vacuum-deposited thin-film standards of known concentrations in ng/cm^2. The neutron activation analysis scheme for the aerosol sample consisted of two irradiation periods and three counting periods. In the first irradiation period, Cl_2, Br_2, and nine other elements were determined by direct comparison to irradiated standards. In the second irradiation stage and after a decay period of

7 days, Br_2 was determined. Finally a decay period of 30 days allowed the determination of other elements.

The error (> 10%) in the quantitative determination of bromine by the x-ray fluorescence method is ascribed to the self-absorption of x-rays in the particulate deposit and the collection substrate. The largest errors in the determination of elemental content per unit volume of air in both methods are ascribed to uncertainties in the filtration process itself, such as air volume measurement, filter efficiency, and filter loading effects. The authors reported that the results of these two techniques agree but no correlation between them was given.

Hammerle et al. (31) compared the results obtained with x-ray fluorescence and neutron activation analyses and found that the two methods agreed with each other within 20% in the determination of Br_2 and nine other elements in aerosol samples. They used Mo-K as the excitation soruce in the x-ray fluorescence determination. They suggested that the limit of detection could be further improved by increasing the flow rate of air through the filter (> 16 L/min) and by increasing the collection time (> 24 hours).

Artz and Chessin (32) applied this technique to determine the Br_2 concentration in aerosols, using a calibration plot obtained with known concentrations of bromine deposited on Whatman # 41 filter paper. The use of a chromium x-ray tube (50 KV and 30 mA) and a sample holder of 2 cm radius in this technique yielded a sensitivity of 4.3 ± 0.5 cps/μg, with a limit of detection of 0.88 μg of bromine. In this determination, LiF was used as the analyzing crystal in the wavelength dispersion of x-rays

Stoeppler et al. (33) used a portable continuous gas analyzer based on x-ray fluorescence to monitor SO_2, HCl, and Cl_2 in the exhaust gases of industrial furnaces and chemical production plants. The sample of air to be analyzed was mixed with a stream of H_2, which acted as a carrier gas, and flushed into the space between two windows adjoining a proportional counter and a lead-shielded radiation source.

For the ^{3}H-Ti source having radioactivity of 2.5 Ci, the detection limit was of the order of 0.1%. These authors recommend the use of a radioactive source containing more ^{3}H and larger windows on the proportional counter to improve the detection limit and to shorten the measurement time.

Bozai et al. (34) collected a sample of bromine in air on Whatman # 42 filter paper by passing air at a flow rate of 7-9 L/min over a period of 7-14 days. The sample was then enclosed in Mylar and sealed, to avoid evaporation. The analytical method used was based on the detection of characteristic K and L x-rays induced by the K x-rays of ^{241}Am-I source target assembly. A Si(Li) diode with a Be window was used for detection. They found that samples collected at atmospheric heights of 1.5 and 15 m had the same elemental composition, whereas samples collected on consecutive filters showed sharp elemental fractionation. Though these authors did not report the sensitivity and limit of detection, they suggest a more powerful radiation source and a longer sampling period to improve the limit of detection.

Verbeke et al. (35) used energy-dispersive x-ray fluorescence analysis for S, Cl_2, K, and Ca in aerosols. In this multi-element determination, the sample collected on Whatman # 41 filters was analyzed with Ti-K alpha x-rays as the excitation source and a multichannel analyzer. The net peak intensity of each element was calculated by two methods: (1) subtracting from the counts at the peak maximum of each element, a contribution from the background and another from the influence of other spectral components, and (2) assuming the peaks are approximately gaussian in shape, use of iterative least-squares fitting of data to obtain net peak intensities. The latter provided more precise results, with a sensitivity of 6.6 counts/µg of chlorine. The chlorine content of the filter by this method was found to be lower than that obtained by neutron activation analysis of the same filter, due mainly to the gaseous diffusion of chlorine.

2.5 Radiochemical Determinations

2.5.(a) Measurement of the Natural Radioactivity of the Sample

Among the halogens, the radioactive isotopes of iodine are by far the most common radioactive air pollutants. The principal isotope encountered is ^{131}I. Since iodine is readily volatile in elemental form, it is released continuously in nuclear reactors, during the processing of spent reactor fuels and in explosions of nuclear devices. The most widely used method for the collection of iodine from air is by adsorption on activated charcoal. The samples are then analyzed by placing the adsorber directly on a scintillation crystal for beta counting or in a well counter for gamma counting

Fukuda et al. (36) reported obtaining a collection efficiency of 75% on activated charcoal during a sampling period of 24 hours even under high-humidity conditions. Using a Geiger-Müller (GM) counter tube detector-collector assembly, Block et al. (37) detected a minimum activity of 9×10^{-9} μCi/cm^3 of ^{131}I in air after a collection period of 10 min.

Brauer and Kaye (38) were able to reach a limit of detection of 0.02 disintegrations per minute (d.p.m.) for I_2 in air, using beta-gated gamma ray spectrometry. Adams (39) employing a GM counter tube assembly was able to determine iodine in air with an error of 15% over the range of 10 to 10^6 dpm (30 mCi to 200 Ci), with a collection efficiency of 99.99% of ^{131}I on charcoal.

Goldstein et al. (40) used a Ge(Li) detector to achieve a limit of detection of 3×10^{-15} μCi of ^{131}I in air with a standard deviation of 7%.

2.5.(b) Instrumental Neutron Activation Analysis

This type of radioactivity-based analysis is performed by measuring the activity (beta and gamma rays) of a sample that has been irradiated with thermal neutrons. The quantitative relation for an isotope nuclide that is made radioactive is given by

$$A = N \cdot f \cdot \sigma \cdot s$$

where A is the amount of radioactivity in disintegrations per second (dps), N is the number of atoms on the target nuclide, f is the neutron flux ($n \cdot cm^{-2} \cdot sec^{-1}$), σ is the thermal neutron cross-section for the nuclear reaction (barn (10^{-24} cm^2)) and s is the saturation factor. Radioactive elements begin to disintegrate immediately after they are formed. Therefore, the apparent amount of the product is related to the half-life of the nuclide formed. This is given by the saturation factor, s.

$$s = 1 - e^{-\lambda t_i}$$

where λ is the disintegration constant for the radionuclide formed and t_i is the irradiation time (sec). As the irradiation becomes longer, s increases and approaches unity. Short-lived halogen nuclides are formed efficiently by short irradiation and decay quickly. In these nuclides, high analytical sensitivity is obtained by measuring the activity after a short time of irradiation. The types of counting equipment generally used are: (1) scintillation counters, (2) NaI (Tl) crystal, and (3) semiconductor detectors (e.g., Ge(Li) detector). Though the scintillation counters are more sensitive than the semiconductor detectors, they lack resolution. The latter are commonly employed in multi-element analysis.

In general, ^{37}Cl, ^{80}Br, and ^{127}I isotopes in the samples are irradiated with thermal neutrons for 5 min and cooled for 15 min, and their activities are measured for 1000 sec. Fluorine is not determined with this technique since ^{16}N and ^{20}F produced have very short half-lives.

This technique is found to be useful for the non-destructive determination of elements at the sub-ppm level, with reliable accuracy and precision. A fundamental limitation of this method, like other nuclear ones, is its inability to distinguish among different oxidation states of an element. It also suffers from possible interferences and matrix effects.

Rahn, Borys, and Duce (41) developed a sampling scheme for determination of gaseous and particulate halogens in air. Halogens associated with particulate matter are first removed from an air stream by filtration with Nucleopore (cellulose ester) filters. Next, inorganic gases containing halogens are removed with three Whatman # 41 filters impregnated with a 10% (W/W) solution of tetrabutylammonium hydroxide (TBAH) in a 10% (v/v) glycerol-water mixture; this is followed by several beds of activated charcoal to absorb organic halogen gases. The impregnating agent in the filter paper reacts with the halogens and retains the products:

$$X_2 + 2OH^- = X^- + OX^- + H_2O$$

The filter paper is then irradiated with thermal neutrons (flux: $4 \times 10^{12}\ n\cdot cm^{-2}\cdot sec^{-1}$) for about 20 min. After the sample is set to cool for 6 min, the decay is monitored for 800 sec with a Ge(Li)-gamma ray detector coupled to a multichannel analyzer. The amount of halogens in the sample is calculated by comparing with irradiations of standard halogen mixtures spotted onto Whatman filters. Photopeaks used for calculations are 1643 KeV for ^{38}Cl, 617 KeV for ^{80}Br, and 443 KeV for ^{128}I. Obviously, this type of determination of halogens could not give accurate results for the free elements since TBAH would also retain hydrogen halides present in the sample:

$$HX + OH^- = X^- + H_2O$$

Hendryx, and Dams (42) evaluated the error distribution in the determination of chlorine, bromine, iodine, and eight other elements in air samples. Aerosols were collected simultaneously on four identical Whatman # 41 filters in one location, using two different high-volume air pumps. The four filters were quartered and the concentrations of the elements determined in triplicate on all 16 quarters by neutron activation analysis. For this purpose the sample was irradiated with a neutron flux of 10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$ for 5 minutes. After 3 min decay, the activity was counted for 6 minutes with a Ge(Li) detector. Fifteen minutes after the end of the irradiation, the sample was again counted for 20 min. They observed that variations in reading the flow rate and computing the total volume of air contributed significantly to the uncertainty of the results.

Gray et al. (43) collected the halogens in air on Millipore filters and analyzed for chlorine and bromine with a neutron flux of 5×10^{13} $n \cdot cm^{-2} \cdot sec^{-1}$ and a Ge(Li) detector. Gamma rays of 1642 KeV energy from ^{38}Cl (from 1 min irradiation and 15 min decay) and 554.3 KeV energy from ^{82}Br (from 1 hr irradiation and 20 hrs decay) were monitored.

Pillay and Thomas (44), Bogen (45), and Obrusnik et al. (46) determined the halogens in air with similar procedures and with an error of 25%. Janssens (47) determined bromine along with uranium, cobalt, indium, and antimony collected from air with Whatman 41 filter paper, with a standard deviation of 2.8% for bromine.

2.5.(c) Radiochemical Neutron Activation Analysis (R.N.A.A.)

In this technique, a chemical manipulation is performed on the sample between the stages of (i) irradiation and cooling, and (ii) counting. A precipitant or a carrier for the element to be determined is added to the sample after irradiation. The carrier is equilibrated with the element in the sample by fusing the latter with Na_2O_2 or treating with strong acid or alkali. Then the element of interest is separated along with the carrier and the radioactivity is measured.

This technique is employed to measure the radioactivity of the required element free from the interferences of other radioactive nuclides present in the sample.

^{129}I emitted from nuclear fuel processing plants ($t_{\frac{1}{2}}$:1.7 × 10^7 yrs) is much too weak a beta and gamma emitter to permit its radioactivity to be measured. Hence the radiochemical neutron activation analyzes have been performed by McFarland et al. (48). Iodine adsorbed on charcoal was irradiated for 15 min with a neutron flux of 8×10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$. Following the irradiation, the charcoal was leached with concentrated ammonium hydroxide for 15 min. Iodine in solution was then precipitated as PdI_2, and this was washed and mounted for counting. Comparison to a known standard (1-12 μg of iodine) processed in the same way allowed a quantitative determination of ^{129}I. The error in this procedure due to incomplete leaching and counting statistics was estimated as 20% and the limit of detection as 10 ng of iodine.

Iodine, bromine, and chlorine were simultaneously determined by Duce et al. (49), using RNAA, in aqueous atmospheric samples. About 8 mL of an aqueous sample was irradiated with slow neutrons for 20 min. Short-lived isotopes of the halogens were separated using carriers, selective oxidation and reduction, and CCl_4 extraction. The beta activity was counted for solid silver halide sources with a gas flow proportional counter. Seven samples could be analyzed per day with this technique, with an accuracy of 5% and a relative standard deviation of Cl_2 4.3%, Br_2 4.5%, and I_2 4.2%.

Moyers et al. (50) developed a procedure which allows for the isolation, collection, and analysis of atmospheric gaseous bromine and iodine. Particulate matter is removed from the air stream to be sampled by electrostatic precipitation. The gaseous halogen species are adsorbed on activated charcoal. After irradiation of the charcoal sample with thermal neutrons (flux: 5×10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$) for 20 min, bromine and iodine are selectively oxidized (with NaOCl), reduced (with $Na_2S_2O_5$), extracted (with CCl_4), and precipitated as silver halides. The amount of halogens is then determined from the measurement of beta activity of the halide with a gas flow proportional counter. The relative standard deviation of this procedure is 5.3% for bromine, and 3.4% for iodine.

2.5.(d) Radiorelease Method

This approach is based on the chemical reaction of the constituent of interest with a radiolabeled reagent. The labeled component is then released either as a gas or in some readily extractable form. From a measurement of the amount of radioactivity released and the stoichiometry of the reaction, the quantity of constituent of interest can be determined. The chief advantage of this approach is its sensitivity, since highly radioactive reagents are available. However, it suffers from all the limitations inherent in the paricular chemical reaction involved, such as interference from other species. Furthermore, at trace levels quantitative extraction of the released species becomes critical for success.

The chemical displacement reaction,

$$F_2 + 2I^{*-} \rightarrow I_2^{*} + 2F^{-}$$

has been used by Eggebraaten and Miller (51) to measure free fluorine in the atmosphere. A sample of air is drawn through alkali iodide columns tagged with radioactive ^{131}I. Fluorine in air displaces $^{131}I_2$.

The released I_2 is captured in a $Na_2S_2O_3$ solution. The activity of ^{131}I in $Na_2S_2O_3$ solution was measured with a NaI scintillation counter. The limit of detection of this technique was 30 ppb fluorine, which is within the 100 ppb maximum atmospheric contamination limit. Analysis time was 10 min. Discrimination of F_2 from HF can be made by using a NaF column to absorb HF. In addition to interferences from other oxidizing gases, the $K^{131}I$ present on the column is itself a radiation hazard and needs periodic replacement since ^{131}I has a $t_{\frac{1}{2}}$ of 8 days.

2.6 Chromatographic Determinations

Bethea and Meador (52) reviewed the literature for GC columns that had been used for the separation and determination of reactive gases (viz., NO_2, SO_2, Cl_2, F_2, Br_2, HCl, and HF) in air.

2.6.(a) Determination of Fluorine

De Grazio and Auge (53) determined fluorine and oxygen in mixtures by making use of the selectivity of a macroreticular resin towards fluorine. A known volume of F_2-O_2 mixture is split into 2 parts. One part is sent through a chlorofluorocarbon packing which does not retain F_2 or O_2. So the elution peak corresponds to both F_2 and O_2 in the mixture. The other part is sent through a macroreticular resin which retains F_2 and therefore the peak gives the concentration of O_2. The difference in the two peak areas gives the amount of F_2. This method is only useful for batch analysis since continuous flow causes the resin to discolor and evolve undesirable volatiles. Another technique reported to be successful for the continuous analysis of this mixture by the above authors involves the quantitative conversion of F_2 to Cl_2 by reaction with NaCl.

$$2NaCl + F_2 \rightarrow 2NaF + Cl_2$$

The mixture of Cl_2 and O_2 is then sent through a column of Teflon resin coated with 50% Halocarbon Oil, for separation and subsequent detection. This simple and reliable method has a dynamic range of 8 to 100% of F_2. The sensitivity is 0.04 inch peak height/% F_2 with a relative standard deviation of 1 to 8%. Since fluorine attacks tungsten, a nickel filament is used in the thermal conductivity detector, with a loss in sensitivity; therefore it could not be used to determine low concentrations of F_2.

2.6.(b) Determination of Chlorine

Bethea and Meador (52) found from a study of 21 different GC columns that a mixture of H_2S, Cl_2, and SO_2 could be analyzed with either of two columns identified as columns 1 and 2 in Table III. These columns were also effective in making an air-CO_2-NH_3 separation. The specifications of the columns are given in Table III. The retention times are given in Table IV and the peaks in order of elution are given in Table V.

The same authors recommended a three-column system for the analysis of samples containing air and eight acidic gases, NO, CO_2, N_2O, H_2S, HCl, SO_2, Cl_2, and NO_2. The sample would be first sent to column 3. The first peak eluted from the column would be a composite peak of air, NO, CO_2, N_2O, H_2S, and HCl. The second peak eluted would be a composite of SO_2 and Cl_2. The third peak would be NO_2, which could be determined on this column. The first and second composite peaks would be sent to column 1 for the separation of H_2S, SO_2, and Cl_2.

TABLE III

SPECIFICATION OF GC COLUMNS

Col. No.	Partitioning Agent	Solid Support	Mesh	Liquid Loading (%)	Length (ft)
1	Silicone oil SF96	Chromosorb T	40/60	10	10
2	Triacetin	Chromosorb T	40/60	10	10
3	Kel F 90 grease	Chromosorb W AW, DMCS	60/80	10	10

TABLE IV

RETENTION TIME (MIN) OF HALOGENS IN GC COLUMNS

Col. No.	Temp. (°C)	Flow (mLHe/ min)	Inlet Pressure (psig)	Air	CO_2	N_2O	NO	H_2S	SO_2	Cl_2	NH_3
1	32	10	20	2.22	2.60	2.73	2.28	3.25	4.13	6.01	2.83
2	32	10	20	0.73	0.94	0.92	0.73	1.47	9.30	2.34	1.99

TABLE V

PEAKS IN ORDER OR GC ELUTION

Col. No	I	II	III	IV	V	VI
			Peaks			
1	air + NO	$CO_2 + N_2O$	NH_3	H_2S	SO_2	Cl_2
2	air + NO	$CO_2 + N_2O$	H_2S	NH_3	Cl_2	SO_2

The detection limit obtained for chlorine in the separation of a mixture of gases (height to width ratio of 10/1 and 90% or more of baseline resolution) was 300 ppm when using thermal conductivity detection with 1-mL samples. The use of the electron capture detector in place of thermal conductivity detector not only decreased the limit of detection to 0.3 ppm but also increased the amplitude of the signal from 0.51 to 0.8 inch/ppm. Furthermore, the use of a scavenger N_2 flow, which joins the carrier gas between the column and the detector, doubled the sensitivity for Cl_2. The relative analysis error was 10% for Cl_2 for this chromatographic system.

2.6.(c) Determination of Iodine

Sunderman, Howes, and Rosenberg (54) determined atmospheric iodine by passing the sample through a column of $NaHSO_3$ on Chromosorb which is coated with dodecane. Iodine and organic iodides are absorbed and retained by dissolution in the organic film on the particles. Iodine diffuses to the interface between the liquid and the solid phase, reacts with the solid phase to form iodide, and is thus separated from the organic iodides which remain in the dodecane liquid phase. Organic iodides are obtained by the extraction of the organic phase into a solvent. The $NaHSO_3$ particles on dissolution in water give up the iodide they contain. Atmospheric iodine, being mostly ^{131}I, is monitored with a radioactive counter. The separation of iodine from organic iodides is distinct and quantitative since it is based on chemical reactivity rather than adsorptive properties.

2.7 Thermal Conductimetric Determinations

Bresler (55) used a thermal conductivity method to determine the chlorine content in gas mixtures. It has a range of 80-100% Cl_2. This system consists of two Wheatstone bridges (working bridge and comparison bridge). The working bridge consists of two open sensing elements made of Pt (30 ohms) over which the analyte gas flows and two resistances in sealed tubes containing pure Cl_2. The comparison bridge also has two resistances in sealed tubes containing a mixture of 80% Cl_2 and 20% N_2 and two other resistances in sealed tubes with pure Cl_2. Comparison of the potentials of the diagonals of the bridges takes place by automatic balancing carried out on the slidewire of the recording device. The error in measurements is 2%. The measurement range can be varied by altering the composition of the gas mixtures in the sealed tubes and by selecting appropriate current strengths in the two bridges. A flow rate of the sample of more than 100 mL/min is necessary for the steady reading. Sensing elements are immersed in water to ensure uniform temperature of the glass tubes surrounding the resistors.

2.8 Electrochemical Determinations

Electrochemical techniques frequently employed in the determinations of halogens in gaseous samples are coulometry, amperometry, potentiometry, and voltammetry. In most cases the sample is directly trapped in an electrolytic solution; in this manner, the error arising from the inefficiency of a scrubber is eliminated. In some of these techniques, the reagent is regenerated by electrolysis so that the reagent replacement is relatively infrequent. A limitation of this method is that other reducing or oxidizing agents can react in the electrolyte and cause a direct interference. This requires an efficient scrubbing system at the inlet in order to remove the interfering contaminants in the sample. By using the correct scrubbing apparatus and electrolyte, the method can be made very selective to the desired halogen.

2.8.(a) Potentiometric Determinations

Lewis (56) employed a galvanic cell to determine Cl_2 in air. The sensor is designed in such a way that an electrolyte containing 20% NaCl and 0.1% $NaHCO_3$ permeates through an alumina extraction thimble. A silver electrode is immersed in the electrolyte, while a Pt wire electrode is wound about the external surface of the thimble. As the electrolyte moves through the walls of the thimble, a thin electrolyte film is in contact with the Pt electrode on its external surface. Chlorine in air comes into contact with the electrolyte film and dissolves reversibly, establishing quickly an equilibrium concentration, which determines the current measured with a microammeter:

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

The galvanic cell Pt, $Cl_2(g)$ $|NaCl(aq)|$ Ag(s), coupled with the flowing electrolyte, can be used to monitor Cl_2 continuously for more than two months. The cell output is linear up to 3 ppm Cl_2 in air. The Cl_2 sample is drawn through the cell with an aspirating pump at a rate of 200 mL/min.

It is observed that the slower the electrolyte flow, the less responsive the cell to recovery. Since this device is used to monitor unacceptable levels of Cl_2 gas concentrations in air, a faster flow rate of electrolyte is not employed. Used electrolyte from the sensor that gets collected in the sealing reservoir may be pumped to the header reservoir. Thus this device could be converted into a closed-flow analyzer.

2.8.(b) Determinations Based on Electrolysis

Kaye and Grigg (57) used constant-potential coulometry to determine fluorine in air. The apparatus consisted of a bubbler reaching down to a Ag wire cathode at the bottom of the cell and a Pt anode at the top. A 0.1M LiCl is used as the electrolyte. The sensing element is a galvanic cell:

$$Ag_{(s)}\ |AgCl_{(s)}, LiCl_{(aq)},|\ Cl_{2(g)}, Pt$$

It has a spontaneous emf of 0.25 V and is balanced by an external emf of the same magnitude so that no current flows in the absence of fluorine. When a sample containing fluorine is passed into the cell at a flow rate of 70 mL/min, fluorine displaces chlorine from LiCl.

$$2LiCl_{(aq)} + F_2 \rightarrow 2LiF_{(aq)} + Cl_{2(g)}$$

Chlorine formed is reduced at the silver cathode:

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

Insoluble AgCl is produced on the cathode so that the chloride is removed from the reaction. Thus, for every molecule of fluorine, two electrons flow through the coulometric circuit. The concentration of fluorine is determined by the Faraday's law: one g equivalent of chlorine is reduced by one Faraday of electricity. The use of chloride ion in the electrolyte achieves a specificity for the determination of fluorine and avoids interferences from O_3 and NO_2. The output is found to be linear for fluorine concentrations up to 1000 ppm.

Kuempel and Shults (58) described two analytical procedures involving a thin-layer electrochemical cell for monitoring chlorine in air: controlled-potential coulometry and stripping analysis. A thin layer of electrolytic solution containing 0.2 M Na_2SO_4, 0.05 M Na_2HPO_4, and 0.01 M NaH_2PO_4 is used to impregnate a circular piece of filter paper. One side of the filter paper is exposed to the sample and the other side to a Hg pool electrode. A saturated calomel electrode (SCE) and Pt auxiliary electrode are in contact with the solution through the top of the cell. The potential of the mercury electrode is controlled at 0.05 V vs. SCE with a 3-electrode voltammetric set-up. Fresh electrolyte solution is slowly drawn through the filter. An air stream containing chlorine is directed through a hole in the top of the cell. Chlorine is reduced at the Hg electrode and a current-time plot is obtained.

In the stripping analysis mode, the external potential applied to the Hg electrode is switched off. Then an air stream containing Cl_2 is passed through the cell so that Cl_2 reacts directly with Hg:

$$2Hg_{(l)} + Cl_{2(g)} \rightarrow Hg_2Cl_{2(s)}$$

After a measured period of time, the gas stream is cut off, and the potential of Hg electrode is scanned from 0.175 to 0.050 V vs. SCE.

$$Hg_2Cl_{2(s)} + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-$$

Typical current-voltage curves are obtained with this procedure. The area under the voltage-current curve (which is not well defined in the reported (58) figure) was used to determine the amount of chlorine in the sample. The reproducibility of the current responses is about 5% and the limit of detection is 20 ppb. This type of thin-layer cell has the same advantage as the membrane cell in selectivity, and in addition, it also possesses enhanced sensitivity and response time (of 15 sec) owing to the continuous flow of electrolyte solution.

Kane and Young (59) observed that the membrane-type polarographic probe used in the determination of oxygen was less sensitive and slow in response to chlorine gas because of slow diffusion through the membrane. Nevertheless it has been used (59) for semiquantitative determination of chlorine in a mixture of HCl and benzene vapor. The electrolyte used is 15% NaCl solution with fluorinated ethylene-propylene film as the membrane. The 3-electrode cell is found to lose its sensitivity for chlorine after prolonged use (> 96 hrs). To determine low levels of chlorine in HCl and in the atmosphere of a chlorine production plant the same authors (59) used a galvanic probe, in which a silver gauze anode was separated from a Pt cathode by means of a cellulose pad. The probe was soaked in a solution of calcium chloride which being hygroscopic, prevented the electrolyte from drying out. Each determination took about 1 min with a limit of detection of 0.01 ppm. Though this probe responded to O_3 and oxides of nitrogen, it could be used to monitor Cl_2 where the concentration of the interfering gases remained constant.

Dailey (60) developed an amperometric detector for chlorine gas employing a semipermanent electrolyte. It consists of two identicall platinum electrodes immersed in 1-2 mL of a nonvolatile solution of KBr in glycerin; this eliminates the evaporation of electrolyte. The electrodes are polarized by means of an applied d.c. potential of 0.6 V. When the sample containing chlorine comes into contact with potassium bromide, it displaces bromine. At the applied potential bromine is reduced, the electrodes are depolarized and an electrical current proportional to the chlorine concentration flows through the external circuit. When the sampled air contains chlorine at or above 1 ppm, the current developed in the measuring coil exceeds a predetermined value and triggers an alarm. When this occurs, the alarm light flashes and relay contacts are closed to activate fans. The use of a glycerin solution of KBr makes it necessary to change it only once a year. It has a limit of detection of less than 1 ppm of Cl_2 in air. The sensitivity was 1 μA/ppm. Though the detector was designed specifically for chlorine detection, it was found to respond to other oxidizing gases such as ozone, bromine, and chlorine dioxide.

2.9 Titrimetric Determinations

Free iodine is determined titrimetrically with thiosulfate solution, using starch, α-naphthoflavone, or Variamine blue as indicators. Bromine and chlorine are determined indirectly by treating them with excess of KI and titrating the liberated iodine. Iodine and bromine in the presence of one another are determined by utilizing the difference in their reactivity towards formic acid. Bromine readily oxidizes formic acid while iodine does not (61).

$$HCO_2H + Br_2 \rightarrow CO_2 + 2HBr$$

2.10 Summary of Observations on the Methods of Determinations

Among the sixteen methods of determinations of halogens in gaseous samples, emission spectroscopy, phosphorescence, chemiluminescence, mass spectrometry, manometry, and ionometry are less frequently employed. Table VI presents a general summarizing comparison of the limits of detection, the precision of measurement, the analysis time, the advantages and the limitations of all these methods.

2.11 Air Sampling for Halogen Analysis and Its Analytical Difficulties

Sampling of air for halogens determination, as for that of other gases, needs careful attention to avoid the subjecting a modified sample to analysis. A major portion of error observed in the determination of halogens in trace levels is ascribed to three parts of the air sampling procedure: (i) preliminary steps before the collection of air sample, (ii) method of collection and storage of the sample, and (iii) measurement of volume of air sampled.

2.11.(a) Precautions in Air Sampling

Some of the important difficulties encountered in the preliminary

TABLE VI

SUMMARY OF METHODS OF DETERMINATION OF HALOGENS IN GASEOUS SAMPLES

Method	Accuracy *	Precision **	Detection Limit***	Analysis Time (per sample)	Advantages	Limitations
1. UV and Visible Absorptiometry						
a. Colorimetry	4 %	5 %	1 ppb	3-5 min	Fast, simple, and accurate	Reagent instability; interferences
b. UV Absorptiometry	Not available	10 %	0.05 mole %	Continuous	Fast, simple, and accurate	Reagent instability; interferences
c. Reflectance	Not available	Not available	0.1 ppm	Continuous	Fast and simple	Less sensitive; interferences
2. Emission Spectroscopy	15 %	10 %	5.0 ppm	30 min	Free from interferences	Time-consuming and needs skill
3. Raman Spectroscopy	Not available	Not available	0.3 ppm	30 min	Selective	Time-consuming and needs skill
4. X-ray Fluorescence	10 %	12 %	0.1 ppm	15 min	Sensitive; multi-element analysis	Expensive instrumentation
5. Radiochemistry						
a. Natural Radioactivity	15 %	7 %	3×10^{-15} µCi/gm	10 min	Fast and simple	Applicable only to radioisotopes
b. Instrumental Neutron Activation Analysis	25 %	3 %	0.1 ppb	30 min	Sensitive; multi-element analysis	Expensive instrumentation
c. Radiochemical Neutron Activation Analysis	20 %	5 %	10 ng	30 min	Sensitive; free from interferences	Expensive instrumentation
d. Radiorelease	Not available	Not available	30 ppb	10 min	Sensitive	Interference from similar species
6. Gas Chromatography	10 %	8 %	1 ppt	1 min	Fast and simple	Less sensitive for trace analysis
7. Thermal Conductivity	2 %	10 %	80 vol %	1 min	Fast and simple	Nonselective
8. Electrochemistry						
a. Potentiometric	7 %	4 %	0.1 ppm	1 min	Sensitive and continuous	Nonselective
b. Electrolytic	5 %	5 %	20 ppb	15 sec	Sensitive and continuous	Nonselective
9. Titrimetry	12 %	10 %	0.2 ppm	5 min	Fast and simple	Less sensitive for trace analysis

* Relative % error with respect to standards

** Relative % average deviation from the mean

*** $\text{Signal}_{\text{Limit}} = \text{Av. Signal}_{\text{Blank}} + 3\, s_{\text{Blank}}$
where s is the standard deviation of the blank signal

steps of air sampling and the relevant remedial measures are listed in Table VII (62, 63).

TABLE VII

PRECAUTIONS IN AIR SAMPLING

Difficulties	Remedies
1. A density differential between the halogens and air may result in uneven distribution within a stagnant or slow-moving air mass.	Sampling from a turbulent flow or a well mixed air mass.
2. Halogens, being highly energetic, may react with the sampling system, especially particulate filters and moisture traps, or get adsorbed on the walls of tubing.	These pretreatment units should also be analyzed if possible, or evaluated with standard samples.
3. Halogens diffuse through rubber, neoprene, and plasticized PVC tubing	Tubing should be evaluated when the sample is stored for long time.
4. Pressure and temperature fluctuations in the sampling system may affect the halogen content of the sample.	Calibration must be done under identical conditions.
5. Halogens are photochemically active and undergo changes within the sampling system, if they are exposed to light over a long period of time.	Light-sealed containers in the sampling system would eliminate this problem.
6. In continuous monitoring devices, the sampling system must draw continuously a fresh sample of air; i.e., it must not allow the resampling of air which has passed through the system.	An extended exhaust line to a location remote from the sample intake prevents resampling.
7. Inward and outward leakage of stored samples and collection of halogens on the sealing lubricants may modify the sample.	Self-lubricating Teflon joints and stopcocks provide air-tight seals.

2.11.(b) Methods for the Collection of the Air Sample

2.11.(b).1 Adsorption

Adsorption is useful in collecting halogens in air because of its ability to concentrate trace amounts from large volume of air. Commonly used adsorbents are activated charcoal, filter paper, alumina and gas chromatographic support phases such as Chromosorb 102.

Activated charcoal is nonpolar and therefore selective towards halogens and organic compounds and shows little affinity for polar gases such as water vapor. It has moderately large surface area per unit mass and is chemically inert. Its adsorption of halogens is rapid initially but after its small retention capacity has been reached, the gases will be incompletely adsorbed until the carbon becomes saturated and no further adsorption takes place. It is also difficult to desorb the gases quantitatively (47). It is relatively unselective and as such is useful for monitoring some selective nonpolar constituents in air. On the other hand, charcoal does not form radioisotopes to any appreciable extent on irradiation with thermal neutrons and this property makes it suitable for neutron activation analysis for halogens and other elements adsorbed on it (50), in spite of its low collecting efficiency.

Filters are also suited, like charcoal, for determination of the total mass of halogens (gaseous and particulate). Due to the porous nature of the filter, they offer less resistance to air flow than charcoal (30), so that large volumes of air can be sampled for each analysis. They are not affected by humidity changes. Cellulose, glass fibre, and polystyrene (Microsorban) (32) filters collect the halogens mostly in their pores while membrane (cellulose esters) (31) and polycarbonate (Nuclepore) (43) filters collect them predominantly on the surface. As a result, the latter are more efficient by virtue of high retention capacity and desorptive property. In addition, they offer less resistance to air flow and have low levels of hackground impurities and hence are suitable for trace level (sub-ppm) determinations with neutron activation analysis (43) and x-ray fluorescence (48). The use of these filters, in general, produces an error of 10 to 20%, mostly due to the overloading effect. Their collection efficiency ranges from 80 to 100%.

Collection of the halogens from air with charcoal or filters is preferred only when the sample can be subjected to the analysis step without removal, since a complete desorption is nearly impossible.

Chemisorption of halogens on adsorbents such as cellulose filters is made possible by impregnating them with suitable reagents like 4,4'-bisdimethylaminobenzophenone, _o_-tolidine, and tetrabutylammonium hydroxide (23, 24, 29, 36, 41). Some of these reagents are affected by humidity changes in the sampled air and show an overloading effect.

2.11.(b).2 Absorption

Halogens, being less soluble in water than in non-aqueous solvents, are collected with aqueous solutions of suitable absorbents. The collection efficiency of the absorbent is increased by transforming the air stream into small, finely dispersed bubbles with a relatively long contact time through the absorbent. Commonly used absorbers and their characteristics are listed in Table I. Most of these absorbers concentrate the halogens into a small volume of the absorbing solution so that less sensitive analytical techniques can be employed for the determination. The evaporation of the solvent in the absorber over a period of 24 hours contributes about 5% error (15). It can be eliminated by calibrating the analytical method with standard samples under identical conditions. The absorbents used in the collection of halogens in air are given in Table VIII

TABLE VIII

AQUEOUS ABSORBENTS USED IN THE COLLECTION OF HALOGENS IN AIR

Halogen	Absorbent	Efficiency	Error	Comments*
Fluorine	NaOH(aq)	93 - 99%	5-15%	1
Chlorine	Methyl orange(aq)	-	5%	2
	NaOH(aq)	99%	2%	1
	p-Nitroaniline	99%	1%	3
Chlorine, bromine, and iodine	Water	-	5%	4

* 1. Efficiency decreases with time because of absorption of atmospheric carbon dioxide.

2. The color fades slowly after 24 hours, perhaps owing to photochemical decomposition.

3. Interferences from ozone, chloramines, nitrogen dioxide and ammonia.

4. Suitable only for low concentrations of halogens.

2.11.(b).3 Syringe Sampling

This is useful for rapid and convenient sampling of air for halogens

halogens with sensitive analytical techniques or high concentrations of the halogens. Several types of glass and plastic barrel syringes can be used to store gases without significant loss for more than a week. Losses occur, generally from leakage through pinholes and by passage of the gas through interstices on the sealing surfaces. Meador and Bethea (12, 13) used polypropylene syringes to sample chlorine and other gases. However, these syringes require preconditioning with high concentrations of halogens in order to control or minimize the effects of adsorption and reaction with samples. The method offers a simple sampling technique but applications are limited to specific small-volume requirements.

Among other methods of collection, the important ones are: grab sampling and condensation methods. In grab sampling methods, the sample is not concentrated and hence it is more sensitive to contamination by leaks. Again preconditioning is necessary to prevent adsorption losses. The sample is affected by pressure and temperature changes. However, in this method the volume of air sampled need not be known. Condensation methods are complicated by deposition of water vapor and are effective only at low flow rates of air.

2.11.(c) Measurement of the Volume of Air Sampled

The volume-measuring components of an air-sampling system are either volume meters or rate meters. Volume meters, such as the dry test gas meter, measure the total integrated volume that has passed through them for a given period of time by mechanical displacement of an internal bellows by the air flow. The displacement is recorded continuously on a mechanical counter via a series of levers (62). Such meters are accurate to 1% but need proper maintenance and periodic calibration.

Rate meters measure the instantaneous volume flow rate through the sampling system and therefore, have the disadvantage that frequent checks are required to ensure accurate calculation of the total volume sampled. However, they are smaller in size than the dry test gas meter. The common types of rate meters are Venturi meters, orifice meters, flow nozzle meters, and rotameters. In Venturi, orifice, and flor nozzle meters, the measurement of static pressure of an air stream flowing through a constriction allows the calculation of volume of air sampled. The rotameter allows the calculation of flow rate from the position of a float which is acted on by the downward gravitational force and the upward air flow. All these ratemeters, being instantaneous, do not indicate the extent of fluctuation in the air flow and so contribute to the error in volume measurement (42).

Thus, the sampling of air for halogen analysis is as important as the method of analysis itself. In many cases, the error arising from the air sampling is greater than that in the analytical procedure. This can be overcome, at least in part, by calibrating the instrument with standard samples under the same conditions with which the test samples are run.

2.12 Conclusion

Of the several methods available to determine the halogens in gaseous samples, the colorimetric and the electrochemical methods are widely used because of their sensitivity and the need for the use of less expensive instruments, in spite of their susceptibility to interferences from other species. The x-ray fluorescence and the neutron activation analyses are the methods of choice in determining trace amounts (< 1 ppm) of halogens. The potential for multi-element analysis in these two methods makes them useful for monitoring of pollutants, even though they require more time and expensive instrumentation. Titrimetry is preferred for the determination of the halogens present in rather large concentrations (> 100 ppm). It gives fast and reliable results with simple apparatus. Reflectance measurements, being less sensitive, can be used to monitor the halogen contents in gaseous samples where the absolute concentration is not critical. Spectroscopic methods involving lasers as the source of the radiant power find applications in open-path determinations in which the halogens are determined directly, without absorbing them in reagent solutions. This eliminates error arising from the inefficiency of the absorbers and also shortens the analysis time. However, such methods are, at present, complex and expensive. Chemiluminescent determinations are specific, sensitive, and rapid but the reactions involved are not stoichiometric so that careful and regular calibrations are needed. Methods based on thermal conductivity, electrical conductivity, manometry, and ionometry are not selective and hence, only useful to determine the halogens in the absence of other interferences. For the separation and the determination of constituents above 1 ppm level in gaseous samples, the gas chromatographic approach is suitable. Mass spectrometry coupled with gas chromatography is very useful for the quantitative analysis of gaseous samples. The measurement of radioactivity of halogens is the only recourse to monitor radioactive isotopes. This technique is very sensitive and free from chemical interferences.

In short, these methods differ in selectivity, sensitivity, simplicity, and equipment requirements. The selection of the most appropriate method for a given situation depends on the analytical requirements such as the range, sensitivity, overall accuracy, analysis time, and budget for instrumentation.

CHAPTER III

EXPERIMENTAL METHODS AND PROCEDURE

3.1 Apparatus

The spectrophotometric unit used in these studies was a custom-assembled one, a photograph of which is shown in Figure 1. The basic components are:

Light source: 1020-WS tungsten-halogen illumination system (Instrument SA, Inc., Metuchen, NJ), 100-W (24V) Osram lamp.

Monochromator: H-10, Jobin-Yvon concave holographic grating (Instrument SA, Inc., Metuchen, NJ).

Cell chamber and rotary-valve assembly: Custom-made (details are given in Figures 2.1 and 2.2).

Detector: UDT-500 pin silicon photodiode (United Technology, Inc., Santa Monica, CA).

Differential amplifier: Tektronix AM 502 with Tektronix PS 501-1 power supply.

Recorder (Strip-Chart): Sargent SRL.

Interconnection of optical units was accomplished by use of optical outlet-inlet (Cannon) connectors (Pacific Precision Instruments, Concord, CA). The IR photoacoustic spectra were recorded with a Digilab FTS-20C spectrometer (Digilab Inc., Cambridge, MA) and a custom-made cell system. Spectra of samples in solution in the UV-vis region of the spectrum were recorded with a Beckman Model 25 spectrophotometer with Beckman Recorder/Controller (Beckman Inc., Fillerton, CA). In studies to extract rate proportionality constants, the strip-chart recorder was re-

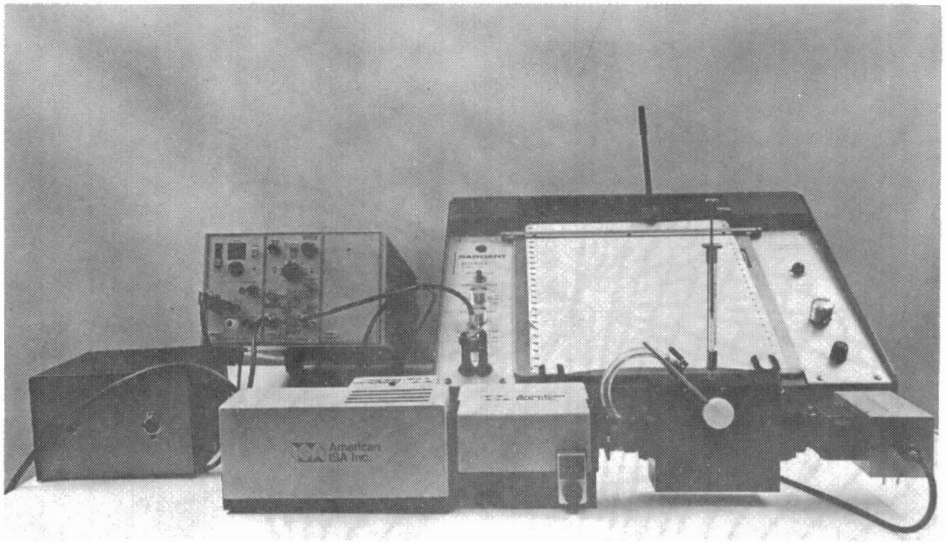


Figure 1. Photograph of Spectrophotometric Unit

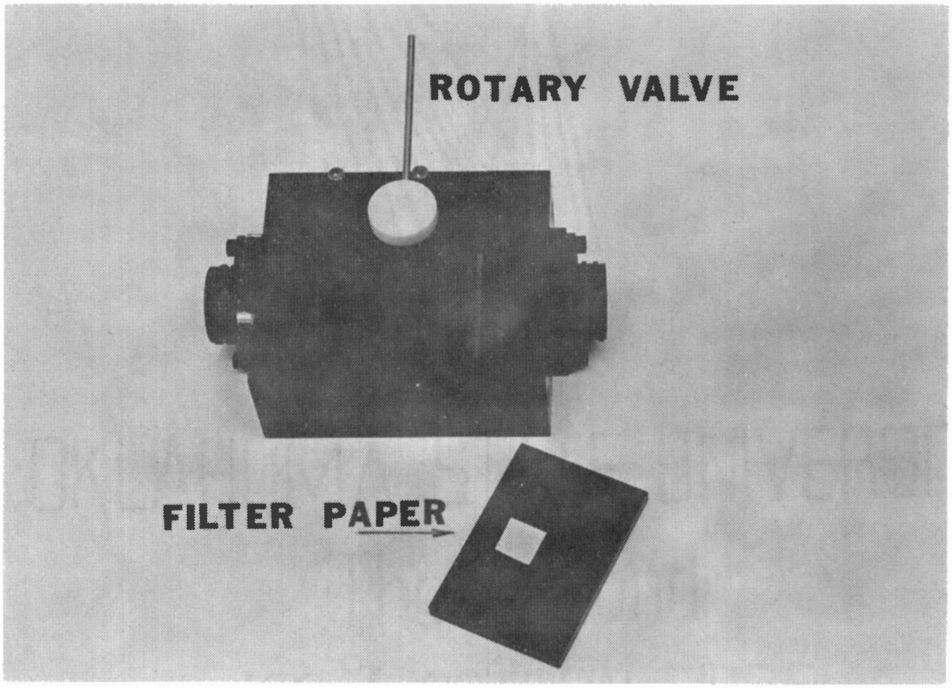
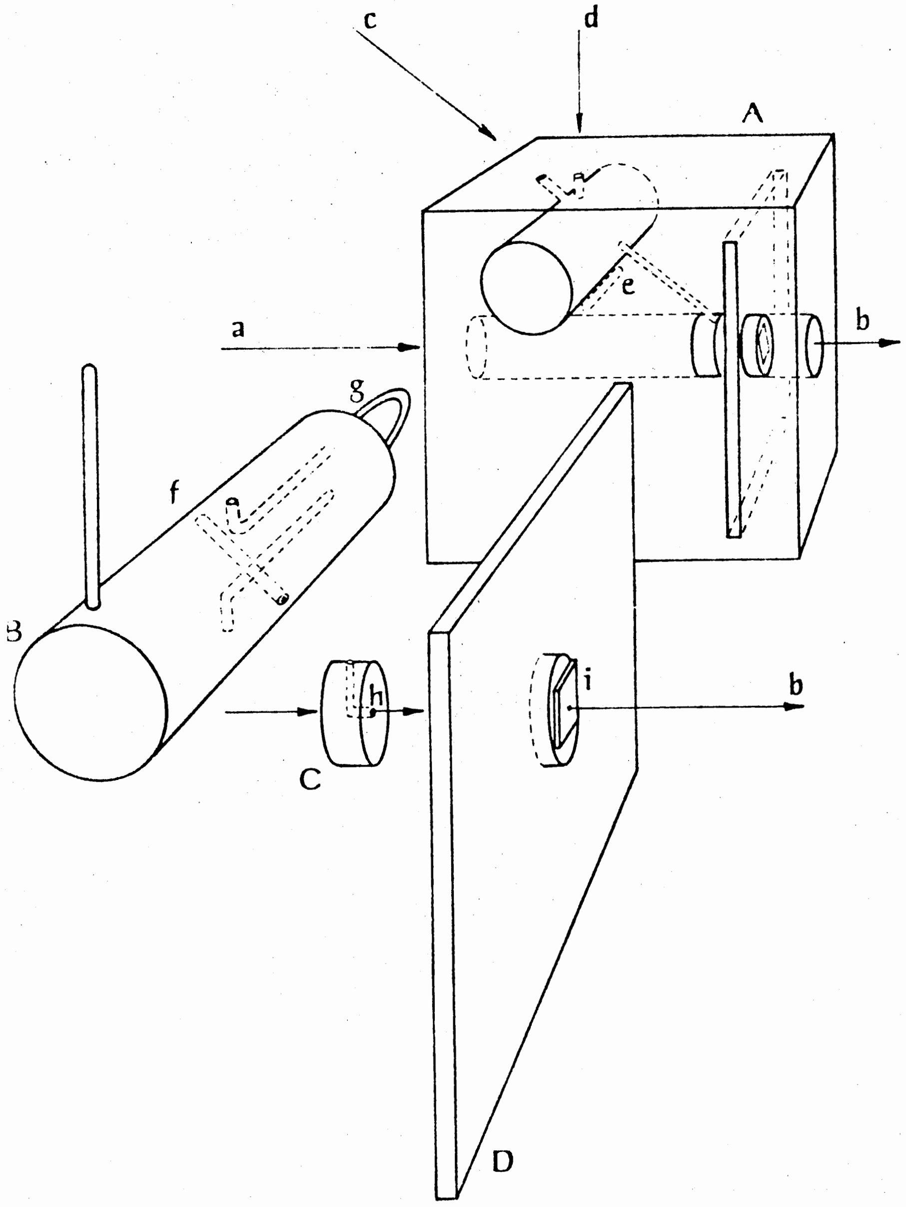


Figure 2.1 Photograph of Cell Chamber and Rotary Valve Assembly



A: Plexiglass Cell Compartment
a: Light Path
b: To Detector
c: Air Inlet
d: Sample Inlet
e: Excess Sample Outlet
B: Rotary Valve

f: Air By-pass
g: Sample Loop
C: Optical Window
h: Pinhole
D: Cell Drawer
i: Filter Paper

Figure 2.2 Schematic Diagram of Cell Chamber and Rotary Valve Assembly placed by a Nicolet 1090A Explorer digital oscilloscope with 94A plugin and Model D amplifier (Nicolet Instrument Corp., Madison, WI).

3.2 Reagents and Solution

A stock solution of 1.00 M arsenic(III) chloride was prepared from 99.8% pure arsenic(III) chloride liquid (Alfa Products, Denvers, MA) and 1.8×10^{-2} M α-naphthoflavone (Aldrich Chem. Co., Milwaukee, WI) in 95% reagent grade ethanol. Required dilutions were made with 1.8×10^{-2} M α-naphthoflavone in 95% ethanol. For Cl_2 determinations 1.00 M arsenic(III) bromide was prepared from arsenic(III) bromide crystals (Alfa Products, Denvers, MA) and 1.8×10^{-2} M α-naphthoflavone in 95% ethanol. Dissolving the arsenic(III) salts in the flavone solution in ethanol resulted in a flocculent precipitate which was then dispersed with the aid of ultrasonic waves (Ultrasonic Cleaner, Cole-Parmer, Chicago, IL) until a clear, yellowish liquid was obtained.

Stock solutions of bromine in air were prepared from liquid bromine (reagent grade, Mallinckrodt, St. Louis, MO) and that of chlorine in air from a lecture bottle (Matheson, East Rutherford, NJ). Both of them were standardized against sodium thiosulfate (64) and used in the preparation of working standards. Stock halogen gases were diluted by injecting 1.00 mL of the stock preparation into a dilution flask (560 mL in volume) fitted with a $\overset{\mathrm{T}}{\mathrm{S}}$ 1 Pyrex stopcock and luer tip.

3.3 Procedure

The solid reagent mixture for reaction was prepared by spotting 0.10 ml of the clear solution containing 0.05 M arsenic(III) and 1.8×10^{-2} $\underline{M}$ α-naphthoflavone in 95% ethanol on a 1.5 cm × 1.5 cm square of filter paper (Whatman, # 541) and drying this on a hot plate at 40°C for about 2 min. The filter paper impregnated with the reagent mixture was then placed on the cell drawer (Figure 2) and inserted into the cell compartment. Compressed air purified by passing through molecular sieves (Type 4A; Linde Division, Union Carbide Corp., NY) was used as a carrier gas at a flow rate of 30 mL/min. The sample loop of the rotary valve was filled with the halogen gas sample (volume: 160 µL) by means of a gas-tight syringe (Precision Sampling Corp., Baton Rouge, LA). Sample injection was accomplished by moving the handle attached to the rotary valve from the upright to a slanting position, so that air stream swept the halogen sample out of the loop and forced it to impinge on the supported reagent mixture. The transient signal was monitored at 520 nm since this wavelength gives the best sensitivity with the instrumental setup used in this study. A back up potential of 300 mV was introduced to bring the signal within the recorder range and then the signal was amplified 200 times and recorded.

CHAPTER IV

RESULTS AND DISCUSSION

The method developed for the repetitive determination of bromine in gaseous samples in an unsegmented continuous-gas-flow system is based on the following chemical reactions:

$$Br_{2(g)} + 2NF_{(s)} \xrightarrow{k_1} 2Br\cdot NF_{(s)} \quad (1)$$

$$2Br\cdot NF_{(s)} + As(III)_{(s)} \xrightarrow{k_2} 2Br^-_{(s)} + As(V)_{(s)} + 2NF_{(s)} \quad (2)$$

in which NF stands for α-naphthoflavone [2-phenyl-4H-naphtho[1,2-b]pyran-4-one]. A gas-solid reaction represented by equation 1 produces the monitored species, the bromine-α-naphthoflavone complex. A solid-solid reaction, represented by equation 2, reduces the trapped bromine to bromide and regenerates the α-naphthoflavone species. Reaction 1 is very fast relative to reaction 2; therefore the overall process from a mechanistic view point can be considered as a series of reactions. These two consecutive reactions generate a transient signal whose height is directly proportional to the amount of bromine gas present in the injected sample.

For the determination of chlorine, the reaction illustrated in equation 3 below is faster than reactions 1 and 2 and precedes them.

$$Cl_{2(g)} + 2Br^-_{(s)} \longrightarrow Br_{2(g)} + 2Cl^-_{(s)} \quad (3)$$

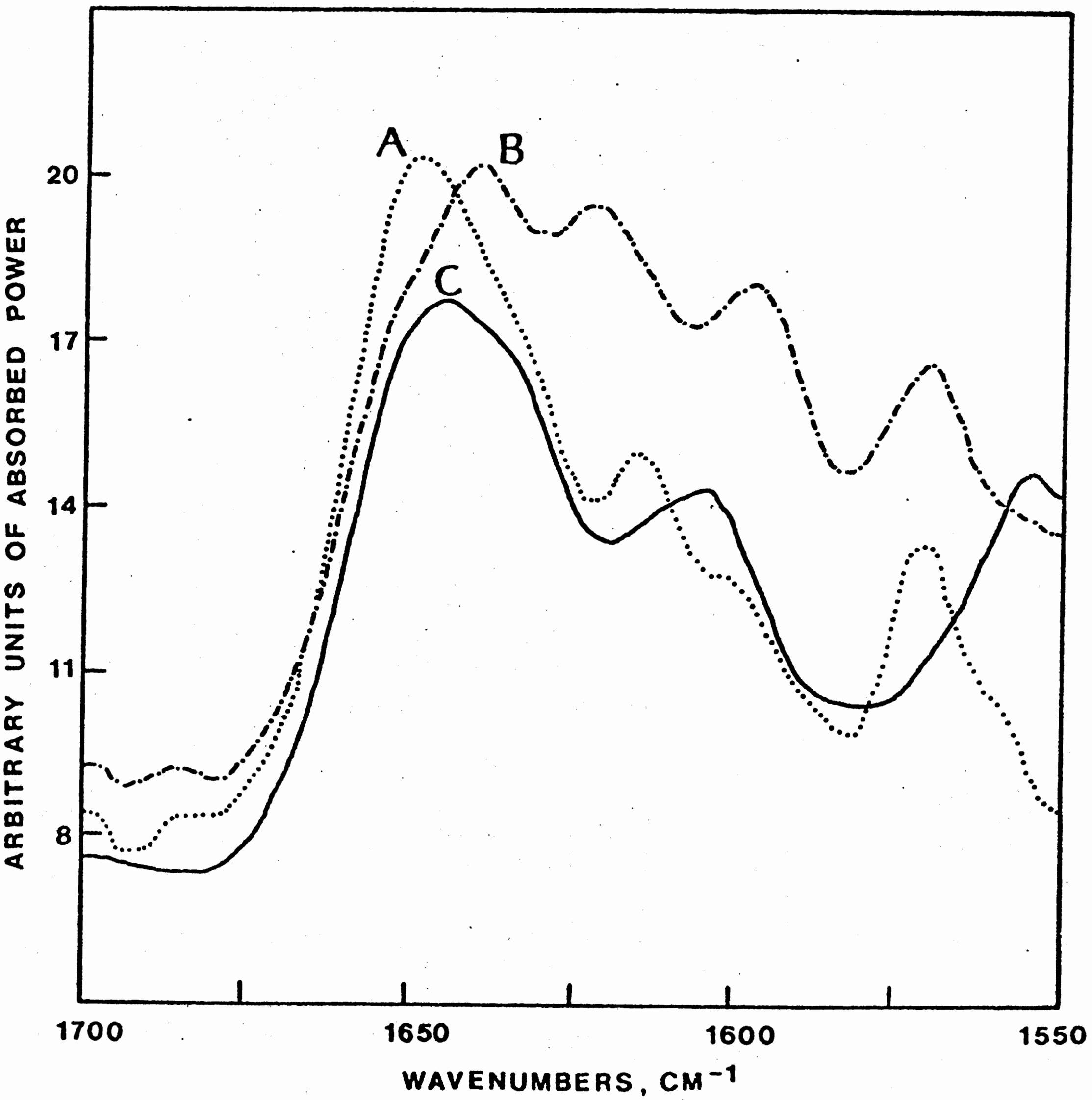
The regeneration of α-naphthoflavone permits repetitive determinations in subsequent samples. The regeneration is also due partly to dissociation of bromine from the complex into the carrier air impinging on the solid surface at which the complex is formed. This desorption process, however, is much slower than the reduction by As(III) and hence its contribution to k_2 is ignored. Though reaction 2 is slower than reaction 1, it is fast enough to permit a large number of determinations per hour. As pointed out by Mottola and Hanna (65) the relative values of the rate proportionality constants, k_1 and k_2 determine the method sensitivity and the determination rate. The use of the values of k_1 and k_2 on the method development is discussed later under the effect of flow rate of carrier gas. The formation and destruction of the red-brown complex is monitored by measuring the intensity of light transmitted through the complex formed on the filter paper. Such direct transmittance photometry is found to be more sensitive with the instrumental set-up used in this study than diffuse reflectance photometry (66) in which the radiation reflected from the surface of a sample is measured. Furthermore, only a simple instrumental set-up is needed for discrete sample analysis, and it is easily adaptable to continuous monitoring.

4.1 The $Br{\cdot}NF_{(s)}$ Complex

α-Naphthoflavone has been used (67) as a reversible indicator for bromate titrimetry owing to its high sensitivity to bromine. According to Belcher (68), its indicator property is based on the adsorption of Br_2 liberated at the end point when this is used in the form of a colloidal suspension in aqueous solutions.

To determine the stoichiometry of the halogen complexes of α-naphthoflavone, the following gravimetric analysis was carried out. A known weight (~ 0.3 g) of solid α-naphthoflavone was exposed to halogen gas/vapor for about 3 min. The excess of halogen was flushed out in a stream of dry air (flow rate of 25 mL/min) at room temperature for about one hr and the resulting complex was weighed. The red-brown product obtained by reacting $Br_{2(g)}$ with solid α-naphthoflavone was found to contain an atom of bromine per molecule of α-naphthoflavone. Iodine vapor similarly produced a 1:1 complex of blue color. Chlorine, on the other hand, either forms no complex or more likely forms an unstable, transient complex, difficult to characterize. Ozone and oxides of nitrogen also do not add on to α-naphthoflavone. The complexes of bromine and iodine slowly release the adsorbed halogen on exposure (~ 24 hrs) to the atmosphere and decompose some what faster above 60°C and in solvents (like ethanol) in which α-naphthoflavone is soluble.

Cramer and Elsching (69) reported a 2:5 ratio for the flavone-iodine species, but they qualified their observations by stating that the ratio was variable. They claimed disappearance of the flavone carbonyl band when ethanolic solutions of α-naphthoflavone and iodine were mixed. However, direct infrared spectroscopy of the solid samples of the bromine and iodine complexes in Nujol mull, obtained with a Beckman IR8 spectrophotometer, failed to show such a disappearance. The infrared photoacoustic spectra of α-naphthoflavone and its complexes with bromine and iodine, (shown in Figure 3) are similar except for the shift of the characteristic carbonyl stretching vibration band at 1650 cm^{-1} in α-naphthoflavone to 1645 cm^{-1} in the bromine complex and to 1640 cm^{-1} in the iodine complex. This shift suggests a very weak interaction typical of ketones with conjugated unsaturation as observed in the benzophenone-iodine system (70), the carbonyl oxygen being the donar site in front of the halogen acceptor. Additional support for this interpretation can be found in x-ray studies of the acetone-bromine



A: α-naphthoflavone, NF

B: I·NF complex

C: Br·NF complex

Figure 3. Photoacoustic Infrared Spectra

system, in which bromine is found to lie colinearly with the C=O bond (71) and in infrared studies of the acetone-iodine system in which the C=O stretching band shifted to lower frequency upon formation of the complex (70). In conjugated ketones such as benzophenone, however, the charge transfer interaction is reported to be very weak (72) and as a result, the shift of C=O stretching band is small, as observed also in the α-naphthoflavone complexes.

Arsenic(III) chloride solution in 95% ethanol has an absorption maximum at 208 nm while α-naphthoflavone in 95% ethanol shows two absorption peaks at 223 and 281 nm. An equimolar (1×10^{-3} M) mixture of arsenic(III) chloride and α-naphthoflavone in 95% ethanol showed no shift in λ_{max} of the individual compounds indicating the absence of any appreciable interaction between them. Photoacoustic infrared spectroscopy of solid samples of α-naphthoflavone, arsenic(III) chloride and their mixture did not provide any evidence of interaction.

According to Mulliken (73), a charge transfer complex (D, A) is formed from a donar (D) species and an acceptor (A) species. This complex exists in two states, the difference in energy between the two being equal to the energy of a quantum at the maximum of the absorption band. In the ground state of the complex the binding between the components is mostly due to the Van der Waals interactions with negligible contribution from electrostatic attraction arising from the transfer of charge from the donar to acceptor, especially in contact charge transfer complexes. In the excited state of the complex the predominant structure is that involving the complete transfer of an electron from D to A.

$$D + A \rightleftharpoons (D,A)\ ,\ (D^{+}A^{-})$$

Between these two states optical transitions are permissible giving rise to the absorption spectrum.

These complexes possess characteristic λ_{max} in the visible or ultraviolet region. Their heats of formation are low (of the order of ~ 1-5 kcal/mole), indicating the weak nature of binding in the ground state of the complex. Contact charge transfer complexes arise out of the collicions between donor and acceptor species and absorption of radiation takes place during the contact interval; hence they have low heats of formation. Their vibrational bands are modified only slightly. Molar absorptivity of these complexes are very high and of the order of 10^4 L/mole·cm and their absorption bands extend over a range of wave length continuously. The breadth of the band again suggests the loose nature of binding in the ground state of the complex. All collected evidence points to the formation of a transitory "contact charge transfer" complex (74) with a structure as illustrated in Figure 4. Solutions of the bromine complex in various solvents such as hexane, carbon disulfide, benzene, 2-propanol, dioxane, isopropyl ether, 1-butanol, and dimethyl sulfoxide were unstable, the red-brown color fading so rapidly as to make recording of the spectrum in the visible region difficult. The absorption spectrum of the bromine complex on filter paper matrix obtained with the instrumental set-up of Figure 1 is given in Figure 5.

4.2 Choice of Solid Support for Chemical Impregnation

The solid support on which α-naphthoflavone and arsenic(III) are to be carried should be thin enough to transmit maximum radiant power and retain a high concentration of reagent mixture even after drying. With

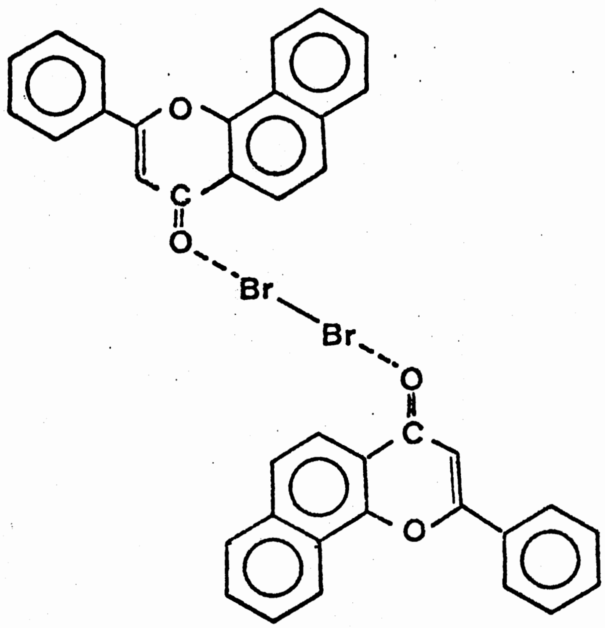


Figure 4. Suggested Structure of α-naphthoflavone-Bromine Complex

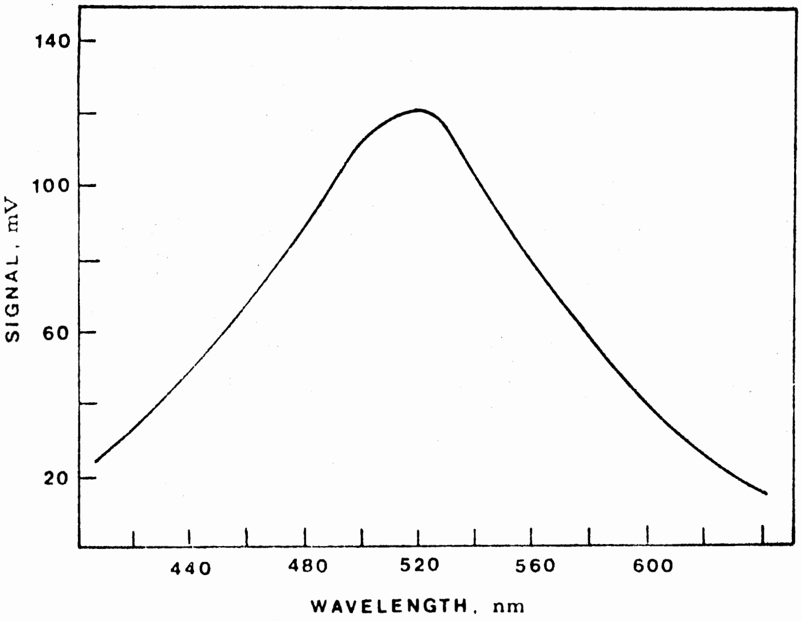


Figure 5. Absorption Spectrum of the Solid Br·NF Complex

this in view, Whatman # 541 filter was chosen from a variety of supports. Other supports such as silica and alumina, which do not provide adequate sensitivity in the transmittance photometry, would be suitable for reflectance photometry. Attempts to deposit the reagent mixture on Plexiglass support were not successful; either a nonuniform film of the reagents or a loose film that peeled off readily from the support was obtained.

4.3 Effect of α-Naphthoflavone Concentration

α-Naphthoflavone in the spotting solution provides the solid reagent matrix on the filter paper. The variation of peak height, S_{max}, for 160 µL of 50 ppm bromine with α-naphthoflavone concentration in the spotting solution of 0.05 $\underline{M}$ arsenic(III) chloride is shown in Figure 6. The concentration of α-naphthoflavone, upto 1.8×10^{-2} $\underline{M}$, is proportional to the peak height and thereafter has negligible effect. Therefore, a concentration of 1.8×10^{-2} $\underline{M}$, which can be easily prepared at room temperature, has been used throughout this work. Concentrations higher than this may extend the range of determination, but they could be realized only at higher temperatures.

4.4 Effect of Arsenic(III) Concentration

For repetitive determinations with maximum determination rate, the time taken by the signal to return to baseline (t_{bas}) should be as short as possible without any significant loss in the signal height (S_{max}). In this system arsenic(III) is involved in reaction 2 which is responsible for the disappearance of the monitored complex. The rate of this reaction, which is dependent on the concentration of arsenic(III),

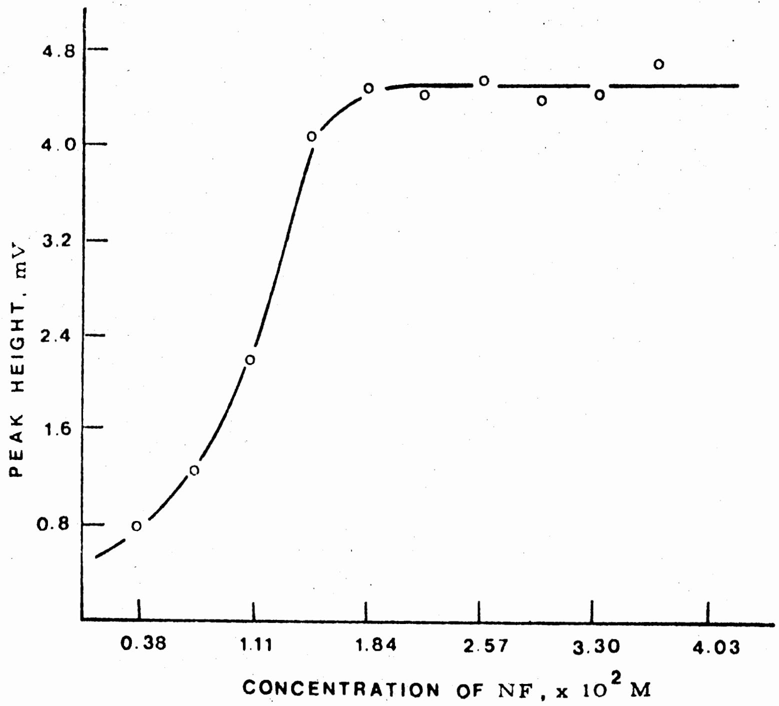


Figure 6. Effect of Concentration of NF on S_{max}

determines the values of S_{max} and t_{bas}: the faster the rate the smaller are these signal parameters and vice versa. Figure 7 shows the effect of arsenic(III) concentration in the spot made from a solution of 1.8×10^{-2} M α-naphthoflavone on both t_{bas} and S_{max}. At 0.050 M arsenic(III), the S_{max}/t_{bas} ratio is maximum and provides the optimum arsenic(III) concentration for repetitive determinations. A concentration larger or smaller than 0.050 M has a greater effect on S_{max} than on

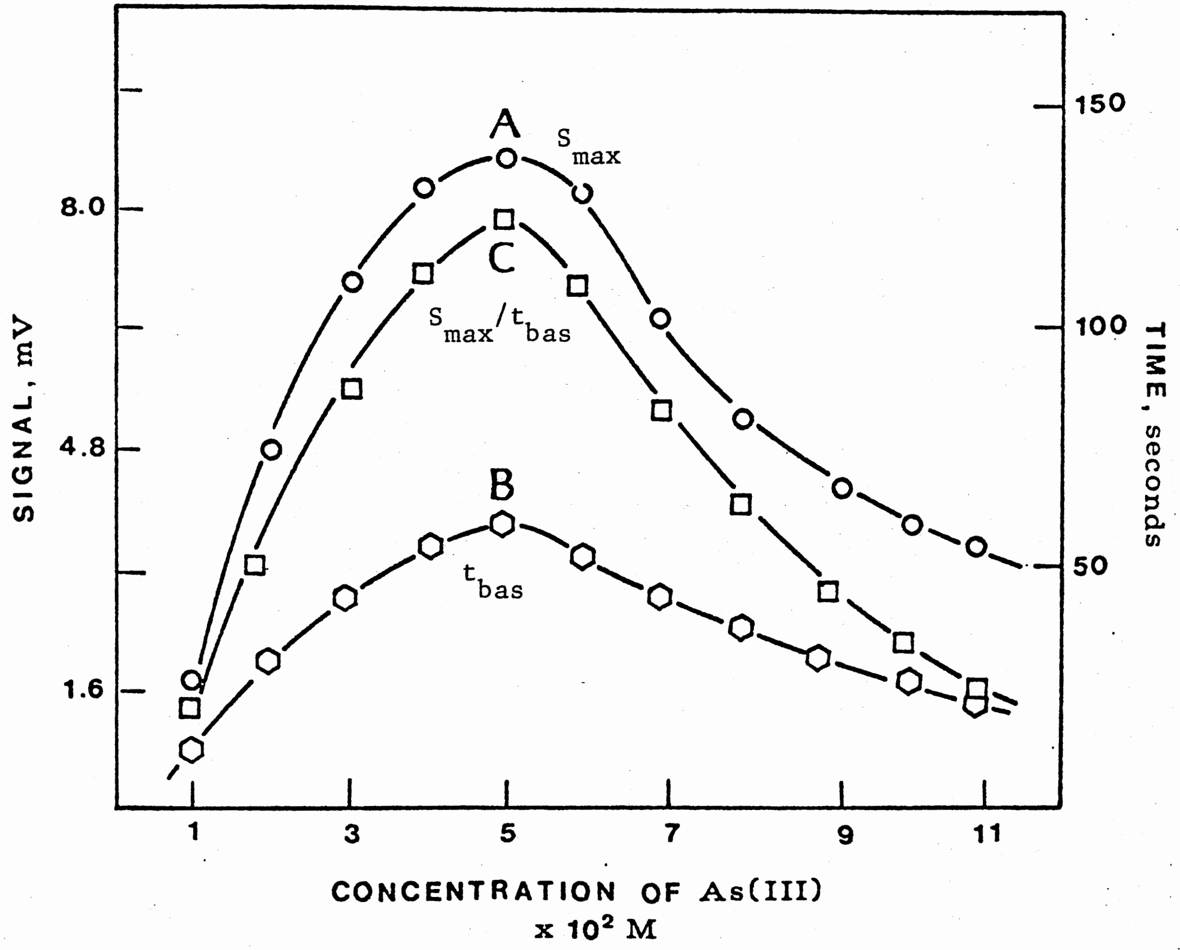


Figure 7. Effect of Concentration of As(III) on the Signal Parameters

t_{bas}, indicating more influence on k_1 than on k_2. The decrease in the value of S_{max} below this concentration of arsenic(III) is contrary to the expected trend. This may be due to change in the nature of the colloidal dispersion of the reagent mixture as the arsenic concentration decreases, so that the drying process produces surfaces with different characteristics for adsorption of bromine. Above 0.050 M arsenic(III), the increased rate of reduction of the complex is responsible for the loss in S_{max}. Thus a concentration of 0.050 M is optimum and allows processing as many as 75 samples before deterioration of S_{max} occurs because of a decrease in arsenic(III) concentration. Repetitive injection of constant amounts of bromine on a freshly prepared surface of the reagent mixture initially **generates** signals of increasing heights. This is probably due to a high local concentration of arsenic(III) on the spot. After five injections, constant S_{max} is realized with also constancy in t_{bas}. This constancy in t_{bas} suggests that the reduction of the complex by arsenic(III) is diffusion controlled. The problem of increasing S_{max} during the initial injections on a freshly prepared surface, however, has been overcome by preliminary exposure of the surface to the vapors of the stock bromine.

The adsorption of iodine by starch is favored by the presence of iodide ions; this effect is described as "polarization" (75). However, the presence of excess bromide ion in the reagent mixture did not increase S_{max}, so that no "polarization" effect was observed.

4.5 Effect of Carrier (Air) Flow Rate

The rate of the carrier gas is another critical variable that affects both method sensitivity (S_{max}) and determination rate (t_{bas}).

An increase in flow rate shortens the time to transport the sample plug from the point of intercalation to the surface on which the consecutive reactions 1 and 2 take place. Simultaneously, such a high flow rate increases the possibility of sweeping the halogen in the sample through the cell so fast that some of its molecules do not react with the reagents on the filterpaper and also favors the decomposition of the Br·NF complex. Thus a compromise flow rate is required to achieve both good sensitivity and limit of detection, and a reasonable determination rate. This optimization problem was analyzed by calculation of the rate proportionality constants k_1 and k_2, the values of which have been shown to dictate sensitivity and determination rate (65).

The rate expressions for reactions 1 and 2 are first order in bromine and the complex respectively, since α-naphthoflavone and arsenic-(III) are present in sufficiently large concentrations that the rates are psuedo-zero order with respect to them. In these series reactions, $k_1 >> k_2$. As a result, the concentration of bromine decreases with time whereas the concentration of the complex increases and reaches a maximum when d[complex]/dt is zero and thereafter decreases exponentially with time. The transient signal which results from monitoring the concentration of the complex has been shown to be useful to extract the rate proportionality constants (65). The fundamental parameters of the transient signal needed for such an evaluation, as shown in Appendix B, are S_{max} and the time needed to reach the maximum signal value, t_{max}.

A filter paper square impregnated only with α-naphthoflavone was exposed to a plug of a known concentration of bromine, $[Br_2]_o$, transported by the carrier stream at a very low flow rate (< 2 mL/min). The S_{max} value measured in this case corresponds to the theoretical signal height that would be obtained in the absence of reaction 2. The same concentration of bromine was intercalated into the carrier stream at increasing flow rates so as to impinge on a mixture of α-naphthoflavone and arsenic(III) and S_{max} values were measured at each flow rate. Since bromine and α-naphthoflavone form 1:1 complex, the concentration of the monitored species, $[C]_{max}$ at various flow rates were calculated using the expression:

$$[C]_{max} = \frac{S_{max} \cdot [Br_2]_o}{S_{max(theoretical)}}$$

A knowledge of $[C]_{max}$ allows computation of values for:

$$\beta_{max} = [C]_{max}/[Br_2]_o$$

which in turn permits calculation of κ from $\beta_{max} = \kappa^{\kappa/(1-\kappa)}$. Substitution of κ in

$$\tau_{max} = \ln(\kappa)/(\kappa-1)$$

allows evaluation of k_1 from $\tau_{max} = k_1 \cdot t_{max}$. Finally, k_2 can be obtained from $\kappa = k_2/k_1$. This method, referred to as Method I in Appendix B, is used to obtain the values of k_1 and k_2. Method II is based on the steady-state approximation and it permits calculating k_2 from

$$\beta_{max} = e^{-k_2 \cdot t_{max}}$$

The value of k_1 can be arrived from κ.

These two methods (Methods I and II) give the same values of k_1 and k_2 for a given set of signal parameters because the value of β_{max} is above 0.4 and in the range of 0.69-0.82.

Table IX summarizes the calculation of k_1 and k_2 from the signal profiles at different flow rates of carrier gas. Figure 8 illustrates the variation of the rate proportionality constants at different flow rates. The value of k_1 increases steadily with an increase in flow rate, suggesting that an increased flow rate mainly shortens the time needed for the molecules of bromine to reach the reaction site and sweeping of halogen from the cell is negligible in the range of flow rates studied. The insignificant change in k_2 with flow rate also confirms the minimal sweeping effect. Evidently, the return to baseline is controlled mainly by the rate of reaction 2, which remains constant since the concentration of arsenic(III) is effectively constant.

TABLE IX

CALCULATION OF k_1 AND k_2 FROM THE SIGNAL PARAMETERS
AT VARIOUS FLOW RATES OF CARRIER GAS

Flow Rate (mL/min)	S_{max} (mV)	C_{max} (mM)	t_{max} (sec)	k_1 (sec^{-1})	$k_2 \cdot 10^2$ (sec^{-1})
10	37.06	1.76	1.93	1.12	1.87
20	42.04	1.99	1.03	2.64	2.18
30	43.73	2.07	0.88	3.29	2.20
40	42.13	2.00	0.67	4.00	3.44
50	40.53	1.92	0.50	4.99	5.38

$[Br_2]_o$: 2.52 mM; $S_{max(theoretical)}$: 53.06 mV

The ratio of S_{max} to t_{bas} increases slightly in going from 10 mL/min to 40 mL/min flow of carrier gas with a significant increase in determination rate, a flow rate of 30 mL/min is then chosen as the optimum flow. It is of interest to note that at 10 mL/min the determination rate per hour is 60 but at 30 mL/min it is close to 120.

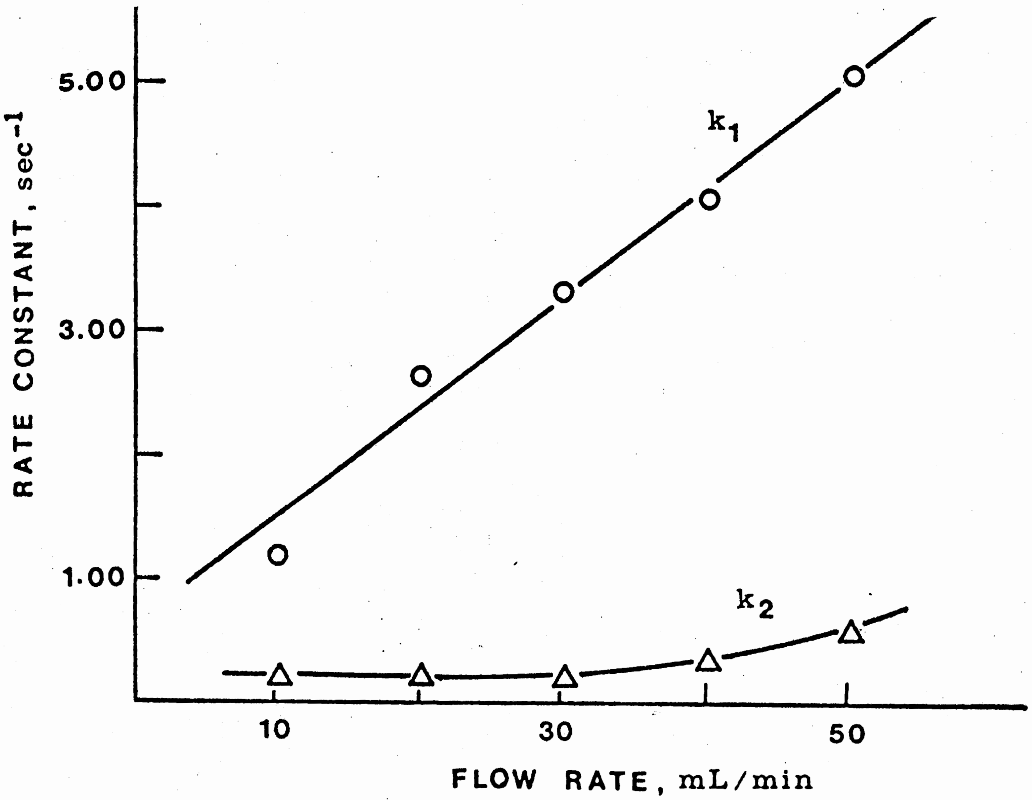


Figure 8. Effect of Flow Rate of Carrier Gas (Air) on Rate Proportionality Constants

4.6 Effect of Sample Size and Point of Injection

Injection of the halogen-containing sample at increasing distance from the reaction zone delays the appearance of the peak corresponding to the first injection and produces broader peaks (longer t_{bas}) as a result of dispersion. As shown in Figure 9 and as expected, S_{max} increases with sample size; similar trends are observed with t_{max} and t_{bas} even when the injection point is only 2 cm from the reaction zone, as illustrated in Figure 9. Since this distance is small, longitudinal sample dispersion is minimal. Radial dispersion or rapid adsorption-desorption of halogen on the walls of the sample loop seems responsible for the observed increase in t_{max} and t_{bas}. The overall shape of the peak suggests convection-controlled dispersion in the sample loop (76).

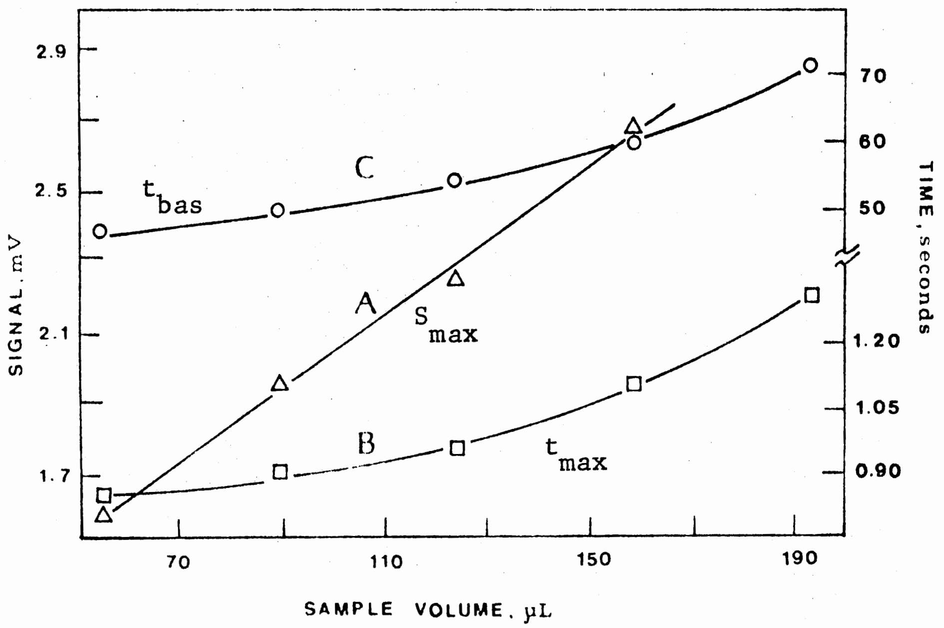


Figure 9. Effect of Sample Size on S_{max}, t_{bas}, and t_{max}

4.7 Working Curve, Limit of Detection, and Sensitivity

Under the above experimental conditions, straight-line plots, as shown in Figure 10, were obtained up to 100 ppm of either bromine or chlorine. Concentrations greater than 100 ppm caused deviation from linearity and S_{max} values became more or less constant above 200 ppm.

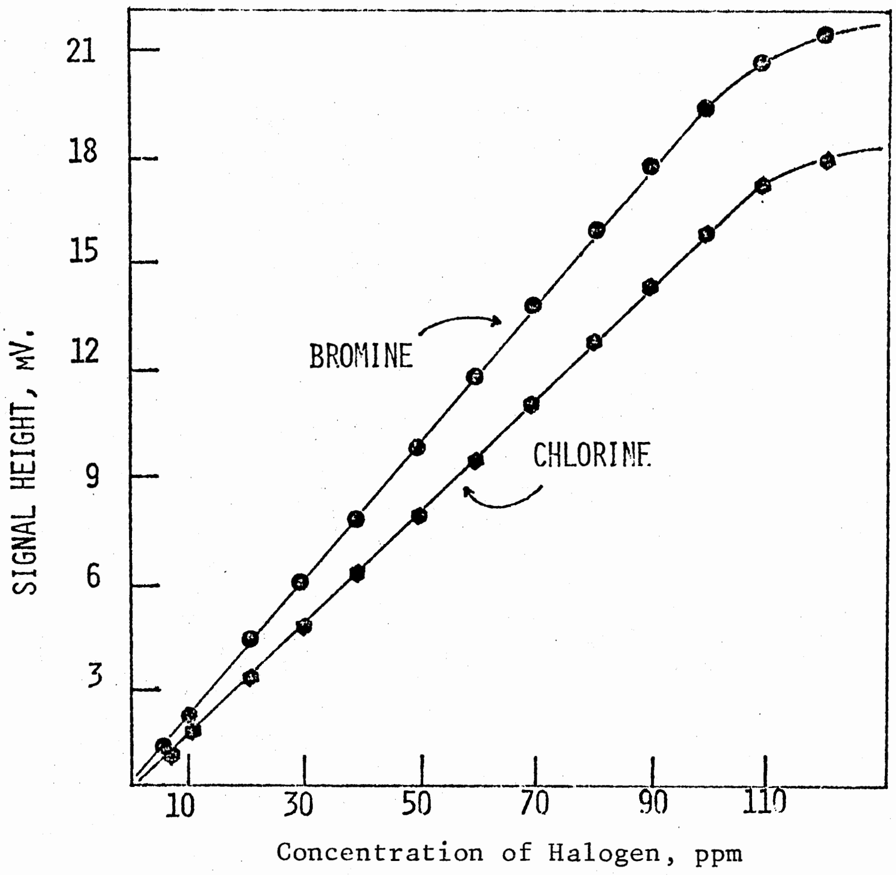


Figure 10. Working Curve for the Determination of Bromine and Chlorine

This is probably due to multilayer accumulation of halogen molecules and saturation of the reaction site. Reproducibility of the method was tested by repetitive injections of 160 μL of 25 ppm bromine and chlorine. The limit of detection, sensitivity, and the relative standard deviation in measurement are given in Table X. Typical signal profiles for bromine and chlorine injection are shown in Figures 11 and 12 respectively. The irregular and slow return of the signal to baseline depicted in Figures 11 and 12 shows that diffusion in the solid support takes place, as expected, intrinsically more slowly than in liquid phase. Injection of chlorine leads to similar signals. Presence of ozone upto 50 ppm in the samples of bromine in air did not affect the S_{max} values and hence ozone is expected to show no interference in this determination.

TABLE X

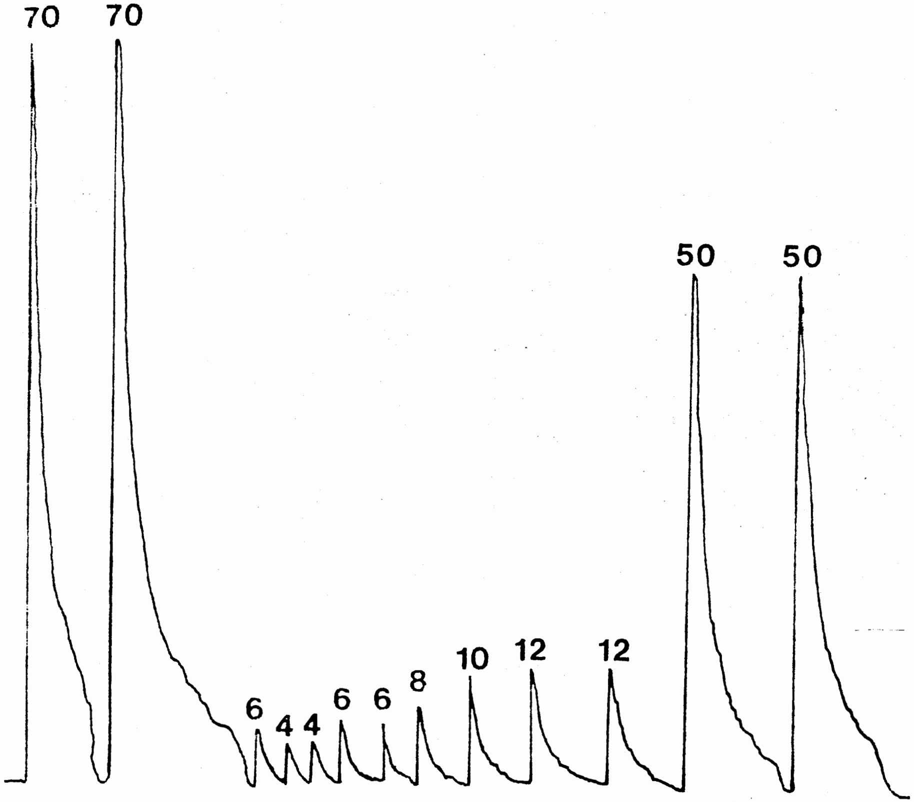
LIMIT OF DETECTION, SENSITIVITY, AND RELATIVE STANDARD DEVIATIONS FOR INJECTIONS OF 25 ppm OF HALOGEN IN A 160 μL SAMPLE

Halogen	Limit of Detection (ppm)[a]	Sensitivity (mV/ppm)[b]	Relative Standard Deviation (%)[c]
Bromine	0.5	2.03	2.8
Chlorine	1.0	1.86	3.0

a. Limit of detection = Average signal for 30 blank injections + 3(standard deviation for the blank)

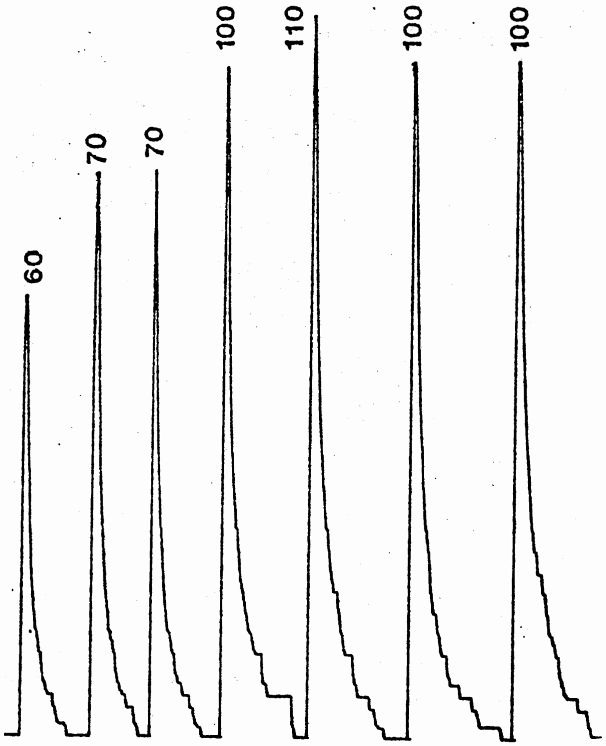
b. Slope of working curve

c. Based on 30 injections without rejecting any value



Number by Each Peak Indicates ppm of Bromine Injected

Figure 11. Typical Signals for Injecting Bromine



Number by Each Peak Indicates ppm of Chlorine Injected

Figure 12. Typical Signals for Injecting Chlorine

CHAPTER V

CONCLUSION

This method demonstrates the possibility of developing analytical techniques based on little used gas-solid interfacial interactions and illustrates its first successful adaptation to an unsegmented continuous-flow analysis involving an all-gas (sample and carrier) system. With proper choice of reagents, the kinetics of series reactions are so modified as to generate a transient signal. The usefulness of the evaluation of the rate proportionality constants of the signal in method development and optimization of experimental parameters is also exemplified in this study. Such a "kinetic optimization" approach proves to be easier and more reliable than other procedures of optimization employed in flow-injection analysis, since it is based on experimentally determinable signal parameters.

The instrumental set-up is simple and modular and can be assembled easily. This method offers competitive limits of detection and sensitivity and high determination rate to adapt either discrete sample treatment or continuous monitoring of gaseous samples in industrial and environmental analyses.

BIBLIOGRAPHY

(1) Ruzicka, J., and Hansen, E. H., Anal. Chim. Acta, 78, 145 (1975).

(2) Skeggs, L. T., Am. J. Clin. Pathol., 13, 451 (1957).

(3) Eswara Dutt, V. V. S., Scheeler, D., and Mottola, H. A., Anal. Chim. Acta, 94, 289 (1977).

(4) Klockow, D., and Teckentrup, A., Intern. J. Environ. Anal. Chem., 8, 137 (1980).

(5) Bryan, R. J., "Measuring, Monitoring, and Surveillance", in Air Pollution; Stern, A. C., Ed., Academic Press, New York, 1976; Vol. 3, Chapter 9.

(6) Stern, A. C., "Air Pollution", Vol. 3, A. C. Stern, Ed., Academic Press, New York, 1976, pp. 368-369.

(7) Boltz, D. F., "Colorimetric Determination of Nonmetals", Inter-Science Publishers, New York, 1958, pp. 165-260.

(8) Otey, M. G., and Pulley, H., Am. Ind. Hyg. Assoc. J., 34, 418 (1973).

(9) Horten, A. D., Thomason, P. F., and Miller, F. J., Anal. Chem., 24, 548 (1952).

(10) Boltz, D. F., "Colorimetric Determination of Nonmetals", Interscience Publishers Inc., 1958, pp. 161-164.

(11) Nicols, P. N. R., Chem. Ind., (London), 39, 1654 (1964).

(12) Meador, M. C., and Bethea, R. M., Environ. Sci. Technol., 4, 853 (1970).

(13) Bethea, R. M., Environ. Sci. Technol., 8, 587 (1974).

(14) Taras, M., Anal. Chem., 19, 342 (1947).

(15) Thompson, C. R., Cralley, L. V., Haff, L. V., Hook, A. W., Schneider, E. J., Strauther, J. D., and Winstein, L. H., Health Lab. Sci., 8, 53 (1971)

(16) Tentative Method of Analysis of Free Chlorine Content of the Atmosphere (Methyl Orange Method), Method 202, in "Methods of Air Sampling and Analysis", M. Klotz, Ed., American

Public Health Association, Washington, D. C., 1977, p 381.

(17) N. I. O. S. H. Manual of Analytical Methods, National Institute for Occupational Safety and Health, Cincinnati, Ohio, 1977, Vol. 1, P. and CAM. 211.

(18) Dharmarajan, V., and Rando, R. J., Am. Ind. Hyg. Assoc. J., 40, 161 (1979).

(19) Gabbay, J., Davidson, M., and Donagi, A. E., Analyst (London), 101, 128 (1976).

(20) Noweir, H. N., and Pfitzer, E. A., Am. Ind. Hyg. Assoc. J., 33, 69, 699 (1972).

(21) Tolg, G., "Ultramicro Elemental Analysis", Wiley-Interscience, New York, 1970, pp. 165-167.

(22) Weber, C. W., and Howard, O. H., Anal. Chem., 35, 1002 (1963).

(23) Denenberg, B. A., and Kriesel, R. S., TAPPI Annu. Meet. Prep., 1976, 33.

(24) Denenberg, B. A., Kriesel, R. S., and Miller, R. W., Int. Conf. Environ. Sensing. Assess. (Proc)., 2, 110 (1975).

(25) Gelman, C., and Young, R. M., Proc. Natl. Anal. Instr. Symp., 8, 179 (1962).

(26) Grove, E. L., and Loske, W. A., Appl. Spectr., 28, 373 (1974).

(27) Burrows, K. M., and Harwood, J. F., Spectrochim. Acta., 19, 17 (1963).

(28) Laane, J., and Krishman, K., U. S. Nat. Tech. Inform. Serv. AD Rep., 1973, 776290/90A; C. A. 81:81853c.

(29) Lorenzen, J. A., Adv. X-Ray Anal., 18, 568 (1975).

(30) Tanner, T. M., Young, J. A., and Cooper, J. A., Chemosphere, 3, 211 (1974).

(31) Hammerle, R. H., Marsh, R. H., Rengan, K., Giaque, R. D., and Jaklevic, J. M., Anal. Chem., 45, 1939 (1973).

(32) Artz, B. E., and Chessin, H., Adv. X-Ray Anal., 17, 225 (1974).

(33) Stoeppler, M., Wisener, L., and Kuehn, W., Radioisotope. Instrum. Ind. Geophysic., Proc. Symp., Warsaw, 1, 147 (1965).

(34) Bozai, M., Gabay, J., Devir, S., and Shenberg, C., J. Radioanal. Chem., 45, 395 (1978).

(35) Verbeke, P., Van Espen, P., and Adams, F., Anal. Chim. Acta, 100, 31 (1978).

(36) Fukuda, S., and Naritomi, M., J. Nucl. Sci. Technol., 7, 450 (1970).

(37) Blocks, S., Beard, E., and Barlow, O., Health Phys., 12, 1609 (1966).

(38) Brauer, F. P., and Kaye, J. H., I. E. E. E. Trans. Nucl. Sci., 21, 496 (1974).

(39) Adams, J. W., U. S. At. Energy Comm., 1964, DP-908, 8p.

(40) Goldstein, N. P., Sun, K. H., and Gonzalez, J. L., Nucl. Technol., 23, 328 (1974).

(41) Rahn, K. A., Borys, R. Y., and Duce, R. A., Air Pollut. Measur. Technique, W. H. O., Geneva, Switzerland, Special Report No. 10.

(42) Heindryckx, R., and Dams, R., Bull. Soc. Chim. Belg., 82, 611 (1973).

(43) Gray, D., Mcknown, D. M., Kay, M., Eichor, M., and Vogt, J. R., I. E. E. E. Trans. Nucl. Sci., 19, 194 (1972).

(44) Pillay, K. K. S., and Thomas, C. C., Jr., J. Radioanal. Chem., 7, 107 (1971).

(45) Bogen, J., Atmos. Environ., 7, 1117 (1973).

(46) Obrusnik, M., Starkova, b., and Blazek, J., J. Radioanal. Chem., 31, 495 (1976).

(47) Janssens, M., Desmet, B., Dams, R., and Hoste, J., J. Radioanal. Chem., 26, 305 (1975).

(48) McFarland, R. C., Walker, D. M., and McLain, M. E., Jr., I. E. E. E. Trans. Nucl. Sci., 21, 503 (1974).

(49) Duce, R. A., and Winchester, J. W., Radiochim. Acta, 4, 100 (1965).

(50) Moyers, J. L., and Duce, R. A., Anal. Chim. Acta, 69, 117 (1974).

(51) Eggebraaten, V. L., and Miller, L. E., Int. J. Appl. Radiat. Isotopes, 18, 183 (1967).

(52) Bethea, R. M., and Meador, M. C., J. Chromatogr. Sci., 7, 655 (1967).

(53) De Grazio, R. P., and Auge, R. G., U. S. At. Energy Comm. Report, REP. 880, 1967, pp. 15.

(54) Sunderman, D. N., Howes, J. E., and Rosenberg, H. S., U. S. At. Energy Comm. BMI-X-10137, 1965, pp. 18.

(55) Bresler, P. I., *Zavodsk. Lab.*, 32, 766 (1966).

(56) Lewis, W. M., *Water Treat. Exam.*, 17, 121 (1968).

(57) Kaye, S., and Griggs, M., *Anal. Chem.*, 40, 2217 (1968)-

(58) Kuempel, G. R., and Shults, W. D., *Anal. Lett.*, 4, 107 (1971).

(59) Kane, P. O., and Young, J. M., *J. Electroanal. Chem.*, 75, 255 (1977).

(60) Dailey, L. L., *Instrum. Aerosp. Ind.*, 21, 447 (1975).

(61) Kolthoff, I. M., and Belcher, R., "*Titration Methods: Oxidation and Reduction Reactions; Volumetric Analysis*", Vol. 3, Interscience Publishers, New York, 1957, pp. 245-246.

(62) R. Perry, and Young, R. J., "*Handbook of Air Pollution Analysis*", Chapman and Hall, New York, 1977, pp. 63-81.

(63) Intersociety Committee, "*Methods of Air Sampling and Analysis*", American Public Health Association, Washington, D. C., 1972, pp. 1-14.

(64) Jacobs, M. B., "*The Analytical Toxicology of Industrial Inorganic Poisons*", Interscience Publishers, New York, 1967, Chap. 15.

(65) Mottola, H. A., and Hanna, A., *Anal. Chim. Acta*, 100, 167 (1978).

(66) Willard, H. H., Merrit, L. L., and Dean, J. A., "*Instrumental Methods of Analysis*", D. Van Nostrand Company, New York, 1974, pp. 101-105.

(67) Bishop, E., "*Indicators*", Bishop, E., Ed., Pergamon Press, New York, 1972, Chapter 8B, p. 667.

(68) Belcher, R., *Anal. Chim. Acta*, 3, 578 (1949).

(69) Cramer, F., and Elsching, G. E., *Chem. Ber.*, 89, 1 (1956).

(70) Bhaskar, K. R., Bhat, S. N., Murthy, A. S. N., and Rao, C. N. R., *Trans. Faraday Soc.*, 62, 788 (1966).

(71) Hassel, O., and Stromme, K. O., *Acta Chem., Scand.*, 13, 275 (1959).

(72) Yamada, H., and Kozima, K., *J. Am. Chem. Soc.*, 82, 1543 (1960).

(73) Mulliken, R. S., *J. Chem. Phys.*, 23, 397 (1955).

(74) Rao, C. N. R., "*Ultra-violet and Visible Spectroscopy-Chemical Applications*", Plenum Press, New York, 1967, pp. 147-163.

(75) Gilbert, G. A., and Marriot, J. V. R., Trans. Faraday Soc., 44, 84, (1948).

(76) Betteridge, D., Anal. Chem., 50, 832A (1978).

APPENDIX A

ADDITIONAL PAPERS OF INTEREST NOT INCLUDED IN THE REVIEW OF METHODS OF DETERMINATION OF HALOGENS IN GASEOUS SAMPLES

Determinations Based on Spectrophotometry

Weinstein, L. H., Mandl, R. H., McCune, D. C., Jacobson, J. S., and Hitchcock, A. E., *Contrib. Boyce Thompson Inst.*, 22, 207 (1963).

Borkowska, M., Strusinski, A., and Wyszynska, M., *Rocz. Panstw. Zakl. Hig.*, 24, 109 (1973); C. A. 79:9364k.

Suvorova, S. N., Vorob'ev, A. M., and Rabovskii, G. V., *Gig. Sanit.*, 28, 48 (1963); C. A. 60:6204h.

Galkina, V. P., and Gertsen, P. P., *Nauch. Tr. Perm. Politekh. Inst.*, 31, 161 (1968); C. A. 71:104907h.

Panin, K. P., *Gig. Sanit.*, 32, 73 (1967); C. A. 68:62458t.

Suvorova, S. N., Vorob'ev, A. H., and Rabovskii, G. V., *Gig. Sanit.*, 29, 65 (1964); C. A. 60:15044f.

Costache, C., and Muica, V., *Farmacia (Bucharest)*, 9, 669 (1961); C. A. 57:3746b

Kochetkova, G. V., and Tsokurenko, I. V., *Pr-vo i Issled. Slekla i Sulikat Materialov*, 6, 271 (1978); C. A. 91:61639r.

Kaszper, W., and Dabrowska, I. K., *Chem. Anal. (Warsaw)*, 9, 1063 (1964); 62:16871d.

Pop, C. S., *Rev. Chim.* (*Bucharest*), 24, 818 (1973); C. A. 81:5925n.

Kettner, H., *Atmos. Environ.*, 3, 215 (1969); C. A. 70:108943u.

Forwerg, W., and Peter, D., *Wasser. Luft. Betrieb.*, 13, 92 (1969); C. A. 71:6356h.

Suzuki, H., and Suzumura, M., *Sangyo. Igaku.*, 19, 495 (1977); C. A. 89: 203169x.

Pacak, P., and Skokanek, M., Chem. Listy., 67, 433 (1973); C. A. 79: 38159c.

Zawadzki, S., and Sojecki, W., Pr. Centi. Inst. Ochr. Pr., 19, 79 (1969); C. A. 71:6347f.

Sojecki, W., Pr. Centi. Inst. Ochr. Pr., 14, 199 (1964); C. A. 62:2170a.

Lada, Z., and Wassak, S., Rev. Chim. (Bucharest), 10, 162 (1959); C. A. 57:7875i.

Teploukhova, G. A., Zavod. Lab., 33, 565 (1967); C. A. 67:113394h.

Parkhomenko, G. V., and Teploukhova, G. V., Tr. Metrol. Inst. S. S. S. R., 96, 158 (1968); C. A. 70:6384w.

Elinson, M. M., Nosava, L. A., and Ovchinnikov, I. M., Zavod. Lab., 39, 272 (1973); C. A., 79:26787t.

Belyakov, A. A., and Kurenko, L. I., U. S. S. R. Patent, 577, 174,25 Oct, 1977; C. A. 89:11400u.

Harptmann, S., Epperlein, J., and Junger, P., Ger. (E) Patent 132, 903, 15 Nov, 1978; C. A. 91:128336k

Kubalski, J., Dynakowski, R., Drygienee, B., and Bartosiak, A., Farm. Pol., 25, 991 (1969); C. A. 73:6924h.

Rykhter, E. V., Shlygina, N. V., and Kobyakina, E. I., Sb. Nauchn.-Prakt. Rabot. Permsk. Obl. Sanit.-Epidemol. St., 3, 48 (1960); C. A. 57:6272i.

Rykhter, E. V., Shlygina, N. V., and Kobyakina, E. I., Sb. Nauchn.-Prakt. Rabot. Permsk. Obl. Sanit.-Epidemol. St., 3, 43 (1960); C. A. 56: 7655h

Varkonyi, T., and Vadasadi, G., Hung. Sci. Instrum., 39, 47 (1977); C. A. 88:176388p.

Gertner, A., Grdinic, V., and Pavisic, D., Acta Pharm. Jugleslav., 18, 167 (1968); C. A. 73:48572x.

Zawadzki, S., Prace. Centr. Inst. Oehrony.-Pracy., 17, 133 (1967); C. A. 67:120002g.

Fuhrmann, H., Staub, 25, 266 (1965); C. A. 64:10303g.

Fuhrmann, H., and Winter, H., Wasser. Luft. Betrieb., 8, 260 (1964); C. A. 63:7628c.

Holzbecher, Z., Kabrt, L., and Tomasek, V., Sb. Vys. Sk. Chem.-Technol. Praze, Anal. Chem. H.11, 161 (1976); C. A. 87:10687q.

Rakov, A. A., *U. S. S. R. Patent* 404, 003, 26 Oct 1973; C. A. 81:41045j.

Panfilova, G. S., and Guseinov, I. A., *Gig. Tr. Prof. Zabol*. 3, 57 (1973); C. A. 79:83039z.

Penchev, N. P., and Kircheva, Z. P., *Godishnik Sofiskiya Univ. Khim. Fak*., 56, 51 (1961-62); C. A. 61:16692d.

Lomonosov, S. A., Shukolyukova, N. I., and Chennoukhova, V. I., *Zh. Anal. Khim*., 28, 2389 (1973); C. A. 81:16302h.

Bresler, P. I., *Zh. Anal. Khim*., 27, 145 (1972); C. A. 76:135315w.

Glasser, L. G., Kanzler, R. J., and Troy, D. J., *U. S. Patent* 3,306,156, 28 Feb, 1967; C. A., 66:101403b.

Hummel, H., and Ebert, J., *Gas Wasserfach*., 104, 1019 (1963).

Determinations Based on Reflectance Measurements

Luebke, D., *Ger. Offen*., 2,534,367, 10 Feb, 1977; C. A. 86:176582f

Derevyanko, D. G., and Zverev, Yu. G., *Nauchn. Raboty Inst. Okhrany Traude, Vses. Tsentr. Soveta. Prof. Soyuzov*., 4, 112 (1964); Ref. Zh. Khim., 101229 (1965).

Agranov, Kh. I., *Nov. Obl. Prom. Sanit. Khim*., 60 (1969); C. A. 71: 116275p.

Agranov, Kh. I., Parfenov, V. N., and Reiman, L. V., *Prib. Sist. Upr*., 9, 40 (1977); C. A. 88:41003p.

Kolesnik, M. I., Sidei, M. M., Boldova, N. N., Bukovskii, M. I., and Lakeeva, T. F., *Zavod. Lab*., 40, 1199 (1974); C. A. 82:34696q.

Bu, C. K., Bak, C. W., and Ryu, O. S., *Punsok Hwakak*., 10, 31 (1972); C. A. 79:9296q.

Grosskoff, K., *Chem.-Ztg*., 87, 270 (1963).

Determinations Based on Spectrometric Techniques

Fujii, Y., and Masumara, T., *Proc. Soc. Photo.-Opt. Instrum. Eng*., 82, 25 (1976); C. A. 86:194130m.

Fujii, Y., and Masumara, T., *Opt. Eng*., 17, 147 (1978); C. A. 89:64133r.

Williams, D. T., and Palm, C. S., *U. S. NTIS*., AD/A Rep., 1974, p.127; C. A. 82:159814h.

Barringer, A. R., *Environ. Pollut. Instrum.*, 1969, p.49; C. A. 76: 6395y.

Determinations Based on Spectrography

Heshmet-Chaaban, G., and Triche, Cl., *Z. Anal. Chem.*, 272, 114-117 (1974).

Macourt, D. J. C., *Ger. Offen.*, 2,732,827, 23 Feb, 1978; C. A. 90:26694n.

Determinations Based on Phosphorescence

Lerener, M. L., *U. S. Patent* 3, 748, 097, 24 Jul, 1973; C. A. 79:73306v.

Determinations Based on Chemiluminescence

Montamart, M., and Gross, M., *Fr. Demande*, 5 Aug, 1977, 2,337,883; C. A. 88:98726f.

Determinations Based on X-ray Fluorescence

Tanemura, T., and Suita, H., *Radioisotopes*, 21, 641 (1972).

Kazimeirz, J., Kazimeirz, O., and Lasa, J., *Nukleonika,* 12, 77 (1967); C. A. 67:70281z.

Dzubay, T. G., and Steyens, R. K., *Joint Conf. Sensing Environ. Pollutants*, *(Proc)*., 1976, p. 211; C. A. 81:34609p.

Sparks, C. J., and Ogle, J. C., *Proc. Annu.-NSF Trace Contam. Conf.*, *1st*., 1974, p. 421; C. A. 80:15003r.

Robinson, D. C., Whitehead, N. E., and Coote, G. E., *Chem. N. Z.*, 38, 81 (1974); C. A. 82:47268b.

Determinations Based on Radioactivity

Deuber, H., and Wilhem, J. G., *Reaktortag*. (*Fachvortr*)., 1977, 813; C. A. 89:79493g.

Wilhem, H., Gerlach, K., and Mahnau, H., *U. S. Patent* 3,864,574, 4 Feb, 1975; C. A. 84:34954p.

Kristova, M., Filev, G., and Vasilev, G., *Nauchni Tr.-Nauchnoizsled. Inst. Radiobiol. Radiats. Khig.*, 5, 221 (1975); C. A. 84:140040x.

Wardaszko, T., *Rep.-Stattl. Zent. Stahlenschutz DDR*, 157, 215 (1974); C. A. 83:197416h.

Finsterwalder, H., Hoffman, W., and Huppert, K. L., *Proc. Semin. Monit. Radioact. Effluents.*, 1974, 203 (1974); C. A. 84:64691t.

Boedege, R., and Gerike, K., *Reaktortagung*, 6th., 1974, 466; C. A. 81: 110770f.

Holfold, R. M., *A. E. C. L. Report*-4595 (1974); C. A. 81:89606r.

Kosmowski, A., *CZ-Chem.-Tech.*, 3, 189 (1974); C. A. 80:89606r.

Godinho, M. M., Teixeira, R., Teixeira, M. R., Bordalo, N. M., Costa, P. E., Faisea, M. C., and De Brito, Q., *Report 1973, L. F. E. N.*-158(B), 44 pp; C. A. 80:102608q.

Krzesniak, J., Zdrojewski, S. Z., Jagielak, J., and Zak, A., *Postepy Fiz. Med.*, 8, 59 (1973); C. A. 82:89701t.

Gerlach, K., *Ger. Offen.*, 2, 143,900, 8 Mar, 1973; C. A. 79:57337a.

Brauer, F. P., Reick, H. G., Jr., and Hooper, R. L., *Phys. Behav. Radioact. Contam. Atmos.*, Proc. Symp., 1973, 351; C. A. 84:8462g.

Wilhelm, J. G., *Atomwirt. Atomtech.*, 18, 297 (1973); C. A., 79:45190j.

Hull, A. P., *Report 1972*, BNL-17303, 14 pp; C. A. 78:150752w.

Racoveanu, N., Herscovici, H., Furnica, G., and Turcitu, E., *Rom. Patent* 53,995, 2 Apr, 1972; C. A. 78:47456d.

Naritomi, M., and Fukuda, S., *Nippon Genshiryoku Gakkaishi*, 14, 531 (1972); C. A. 78:33455r.

Popescu, G., *Rom. Patent* 52,754, 9 Dec, 1971; C. A. 78:23638p.

Nakhutin, I. E., Rastunov, L. N., and Smirnova, N. M., *Contr. Iodine Nucl. Ind.*, Rep. Panel, 79 (1970); C. A. 79:73890b.

Furtado, V. C., *Diss. Abstr. Int.* B 32, 2345 (1971).

Bennett, R. L., Hinds, W. H., and Adams, R. E., *U. S. At. Energy Comm.*, 1968, O. R. N. L.-T-M2071, 43 pp; C. A. 70:24971p.

Holford, R. M., *Treat. Airborne Radioactive Waste*, Proc. Symp., 1968, 7; C. A. 71:76602j.

Lister, B. A. J., *Assessment Airborne Radioactiv.*, Proc. Symp., Vienna, 1967, 37; C. A. 70:31456e.

Ullman, W., *Proc. Symp. Health Phys.*, 2nd Pecs., 1, 183 (1966); C. A. 69:92294z.

Klainer, S. M., *A. E. C. Accession No. 29142. Report No. A. E. D.-CONF.-*66-011-8, 1966; C. A. 68:51465a.

Widell, C. O., *Personal Dosimetry Radiation Accidents*, Proc. Symp. Vienna, 1965, 465; C. A. 67:28576z.

Blanc, A., and Lequasis, J., *Proc. Conf. Nucl. Electron.*, Belgrade, 3, 447 (1961).

Smolkina, T. I., *Sb. Rabot po. Nekotorym Voprosom Dozimetrii Radiometrii Ionizer Izluchenii*, 2, 146 (1961); Ref. Zh., Geofiz., 2B139 (1963).

Mehta, S. K., and Kotrappa, P., *U. S. At. Energy Comm.*, 1961, A. E. E. T. H. P./T. M./2, 19 p.

Determinations Based on Neutron Activation Analysis

Sadasivan, S., and Anandan, J. S., *Indian J. Environ. Health*, 21 10 (1979); C. A. 91:180495a.

Grosch, M., and Wolf, G., *Staub-Reinhalt, Luft*, 38, 47 (1978); C. A. 89: 29879s.

Miller, D. H., Fernandez, S. J., and Rasmussen, R. A., *Radiochem. Radioanal. Lett.*, 30, 235 (1977).

Frana, J., Mastalka, A., and Benes, J., *Jad. Energ.*, 22, 304 (1976); C. A. 86:46809z.

Kirichenko, L. V., Nicolishin, N. Ya., Rustamov, R., and Borisov, N. B., *Tr. Inst. Prikl. Geofiz.*, 21, 43 (1976); C. A. 87:10606n.

Obrusnik, I., *Nukleon*, 1, 25 (1976); C. A. 86:59780h.

Miyamaru, M., and Lima, F. W., *Publ. I. E. A.*, 326, 12 (1974); C. A. 84: 184240s.

Goda, A., Tsuuoka, Y., and Sumi, K., *Bunseki Kagaku*, 23, 63 (1974); C. A. 81:114179t.

Stantroch, J., and Obrusnik, I., *Radioisotopy*, 14, 449 (1973); C. A. 81:53809z.

Dams, R., *Meded. Fac. Landbouwwetensch.*, *Rijksuniv. Gent*, 38, 1869 (1973); C. A. 81:140245f.

Asakuno, K., *Bunseki Kiki*, 10, 563 (1972); C. A. 79:107857t.

Clemente, G. F., *Chim. Ind. (Milan)*, 54, 805 (1972); C. A. 78:19860n.

Muganza, D., and Heindryekx, R., *Rapp. Rech.-Cent. Reg. Etud. Nucl. Kishasa*, 13, 85 (1972); C. A. 85:197207g.

Gorden, G. E., *Int. Symp. Identification Meas. Environ. Pollut.* (*Proc.*), 1971, 138; C. A. 81:86979n.

Determinations Based on Chromatography

Ellis, J. F., and Iveson, G., "*Gas Chromatography*", (Desty, D. H. Ed.), Butterworth Inc., London, 1958, p. 300.

Ellis, J. F., Forrest, C. W., and Allen, P. L., *Anal. Chim. Acta*, 22, 27 (1960).

Cieplinski, E. N., *Application No. GC-DS-003*. The Perkin Elmer Corporation, 1964.

Isabell, R. E., *Anal. Chem.*, 35, 255 (1963).

Ellis, J. F., and Forest, C. W., *J. Inorg. Nucl. Chem.*, 16, 150 (1960).

Millon, J. G., Weber, C. W., and Kuhpen, P. R., *Report No. K-1639*, Oak Ridge Gaseous Diffusion Plant, Nuclear Division, Union Carbide Corp., 1966.

Rochefort, O., *Anal. Chim. Acta*, 29, 350 (1963).

Hamlin, A. G., Iveson, G., and Phillips, T. R., *Anal. Chem.*, 35, 2037 (1963).

Horton, A. D., *Nuclear Sci., Eng.*, 13, 103 (1962).

Huillet, F. D., and Urone, P., *J. Gas Chromatog.*, 4, 249 (1966).

Evrard, E., Thevlin, M., and Joossens, J. V., *Nature*, 193, 59 (1962).

Engelbrecht, A., Nachbaucher, E., and Mayer, E., *J. Chromatog.*, 15, 228 (1964).

Runge, H., *Fresenius Z. Anal. Chem.*, 189, 111 (1962).

Araki, S., Kato, T., and Atobe, T., *Bunsegi Kagaku*, 12, 450 (1963); C. A. 59:10762c.

Cheremukhin, E. P., Kanivetes, Zh. F., and Farefel, E. Ya., *Avtomatich-i Analitich. Kontrol. v. Proiz-Ve Ioda i Broma*, M., 1978, 48; C. A. 91:82518r.

Popp, P., Grosse, H. J., and Oppermenn, G., *Chem. Tech.* (Leipzig), 31, 46 (1979); C. A. 90:109121z.

Determinations Based on Electrical Conductivity

Engelhardt, H., Dechema Monograph, 54, 930 (1965).

Bernard, M. L., and Roux, M., French Patent 2, 131, 388, 15 Dec, 1972; C. A. 79:83045y.

Determinations Based on Electrochemistry

Zalotarev, A. E., Karpovich, L. M., Masalkova, V. P., and Pyarthi, V. M., Metody Anal. Kontrolya. Kach. Prod. Khim. Prom-st., 3, 73 (1978); C. A. 89:162115f.

Ross, J. W., Riseman, J. H., and Kruger, J. A., Pure Appl. Chem., 36, 473 (1973).

Fukuzaki, N., Moriyama, N., Sugai, R., and Ohshina, T., Radioisotopes, 28, 371 (1979).

Schierjott, G., Ger. Offen., 2, 151, 260, 19 Apr, 1973; C. A. 79:13246r.

Hatterer, A., and Hartmann, G., Ind. Chim. Belge., 32, 155 (1967); C. A. 71:9365w.

Waszak, S., Przem. Chem., 12, 221-2 (1973); C. A. 79:132499k.

Ersepke, Z., Chem. Prumysl., 16, 496 (1966); C. A. 66:34511v.

Eaton, M. E., Jr., A. D. Report No. 422659, 80 pp. (1963).

Peters, H. L., Nessim, D. J., Morrow, J. J., and Hilton, G. H., Jr., U. S. Patent 3,471,391, 7 Oct, 1969; C. A. 71:126388s.

Mang, O. K. C., Can. Patent 916,788, 12 Dec, 1972; C. A. 78:16378u.

Yves, C., Genevieve, F., Henri, F., and Grand-Clement, A. M., Ger. Patent 1,798,446, 7 Jun, 1973; C. A. 79:128939m.

Dailey, L., Ger. Offen., 2,455,602, 28 May, 1975; C. A. 83:120330t.

Bamford, R. A., and Dickinson, C. H., Ger. Offen., 2,808,339, 7 Sep, 1978; C. A. 89:170999n.

Soucek, J., Chem. Prumysl., 13, 470 (1963).

Vol'berg, N. Sh., Tr. Gl. Geofiz. Observ., 254, 162 (1971); C. A. 78:61794u.

Tokuda, S., and Takotomi, H., Japan Patent, 7,919,089, 8 Feb, 1979; C. A. 91:9020t.

Dailey, L., *Austral*. *Patent* 497,730, 14 Jan, 1979; C. A. 91:265533e.

Barstow, O. E., and Parth, W. H., *U*. *S*. *Patent* 3,761,376, 25 Sep, 1973; C. A. 79:142652u.

Staszewski, R., Szewezyk, B., Wardencki, W., and Zygmunt, B., *Chem*. *Anal*. *(Warsaw)*., 22, 77 (1977); C. A. 88:181815e.

Novak, J., *Ger*. *Offen* 2,228,184, 21 Dec, 1972; C. A. 78:79397b.

Dow Chemical Co., *Netherlands* *Appl*., 7,310,264, 28 Jan, 1975; C. A. 83: 107899r.

Staszwski, R., and Szewzcyk, B., *Chem*. *Anal*. *(Warsaw)*, 22, 85 (1977); C. A. 88:181816f.

Mueller, T. R., and Fisher, D. J., *O*. *R*. *N*. *L*., T. M. 4813, 1975, pp. 32; C. A. 84:126093k.

Determinations Based on Titrimetry

Shemetikhina, A. A., *Fiz.-Khim*. *Technol*. *Issled*. *Miner*. *Syr'ya*., 116 (1965); C. A. 66:34607f.

Shehirskaya, V. A., Novoe, V., *Obslati*. *Sanit-Khim*. *Analiza*., 204 (1962); C. A. 56:7365a.

Vold'kina, V. G., Grigor'eva, L. N., and Efanova, L. G., *Metody* *Anal*. *Kontroya* *Proizood*. *Khim*. *Prom-Sti*., 10, 87 (1977); C. A. 89:64164b.

Puzankov, N. V., Piskova, N. I., Puzankov, V. V., Kalieva, R. S., and Bespalova, R. P., *Tr*. *Khim.-Met*. *Inst*., *Akad*. *Nauk* *Kaz*. *SSR*., 13, 192 (1972); C. A. 78:118863x.

Starzewski, R., and Zygmunt, B., *Chem*. *Anal*. *(Warsaw)*, 22, 91 (1977); C. A. 88:181817g.

Determinations Based on Manometry

Smale, A., *Vestn*. *Slov*. *Kem*. *Drus*., 13, 9-12 (1966); C. A. 69:40959a.

Determinations Based on Ionometry

Gobrecht, H., Tausend, A., and Sieman, I., *Z*. *Anal*. *Chem*., 199, 81-8 (1964).

Enchevich, I., Petrov, G., Buchvarova, D., and Toderova, V., *Khim*. *Ind*. *(Sofia)*., 49, 445-7 (1977); C. A. 89:11079w.

Gorina, M. Yu., Tr. Metrol. Inst. S. S. S. R., 222, 34-8 (1978); C. A. 90:209251k.

Ross, H., and Hilpus, P., Tartu, Riikliku. Ulik. Toim., 409, 73-83 (1977); C. A. 88:63886f.

Fischer, H., Neufelder, M., and Pruggmayer, D., Fachz. Lab., 18, 214-16 (1974); C. A. 80:53806w.

Determinations Based on Laser Absorptiometry

Hohimer, J. P., and Hargis, P. J., Jr., SAND Report 76-9316 (1977), p. 5; C. A. 88:163364c.

APPENDIX B

KINETIC MODEL OF THE TRANSIENT SIGNAL AND EVALUATION OF RATE PROPORTIONALITY CONSTANTS FROM THE SIGNAL PARAMETERS

(From Reference 65)

The basic scheme for transient signal generation is the operation of two consecutive first-order reactions:

$$A + B \xrightarrow{k_1} C \qquad (1)$$

$$C + X \xrightarrow{k_2} D \qquad (2)$$

Reaction 2 can also be an instrumentally imposed process such as flow that carries the intermediate C in and out of the detection area. If A and X are in large excess, first-order kinetics prevails in both reactions. Therefore,

$$\frac{d[B]}{dt} = -k_1[B] \qquad (3)$$

$$\frac{d[C]}{dt} = k_1[B] - k_2[C] \qquad (4)$$

$$\frac{d[D]}{dt} = k_2[C] \qquad (5)$$

Equation 3 integrates into

$$[B] = [B]_o\, e^{-k_1 t} \tag{6}$$

Substitution of equation 6 in 4 gives

$$\frac{d[C]}{dt} = k_1[B]_o\, e^{-k_1 t} - k_2[C] \tag{7}$$

This, on integration, gives

$$[C] = \frac{[B]_o k_1}{k_2 - k_1}\,(e^{-k_1 t} - e^{-k_2 t}) \tag{8}$$

Let $\beta = \frac{[C]}{[B]_o}$; $\tau = k_1 t$, and $\kappa = k_2/k_1$. Substituting in equation 8 yields

$$\beta = \frac{1}{\kappa - 1}\,(e^{-\tau} - e^{-\kappa\tau}) \tag{9}$$

The concentration of C, as measured by β, goes through a maximum, the position of which depends on κ, relative values of the rate constants. By using equation 9 and setting $d\beta/d\tau = 0$, it can be shown that

$$\tau_{max} = \frac{1}{\kappa - 1}\,\ln(\kappa) \tag{10}$$

and the value of β at the maximum is

$$\beta_{max} = \kappa^{\kappa/(1 - \kappa)} \tag{11}$$

Equation 11 forms the basis of evaluation of the values of k_1 and k_2 from the experimentally determinable parameters: S_{max} and t_{max}. Such a computation can be done by two methods.

Method I: The value of $[C]_{max}$ calculated from S_{max} of the experimentally obtained signal profile and the concentration of the species

$[B]_o$ for which reaction in equation 1 is first order allows calculation of of the value of β_{max};

$$\beta_{max} = [C]_{max} / [B]_o \tag{12}$$

This in turn permits the evaluation of κ from

$$\beta_{max} = \kappa^{\kappa/(1 - \kappa)}$$

Substitution of κ in 10, yields the value of τ_{max}. Since

$$\tau_{max} = k_1 \cdot t_{max} \tag{13}$$

k_1 can be calculated from the known value of t_{max}. Finally, k_2 can be obtained from $\kappa = k_2/k_1$.

Method II: At t_{max}, the net rate of change of [B], $d[B]/dt = 0$. Therefore, its rate of formation is equal to its rate of decomposition.

$$k_1[B] = k_2[C]_{max} \tag{14}$$

Substitution for [B] gives

$$[C]_{max} = (k_1/k_2) \cdot [B]_o \cdot e^{-k_1 \cdot t_{max}} \tag{15}$$

On rearrangement,

$$[C]_{max} = [B]_o \cdot e^{-k_2 \cdot t_{max}} \tag{16}$$

Thus, from the known value of t_{max} of the signal, k_2 can be calculated. The value of k_1 can be obtained from the value of κ.

Limitations of Methods I and II

The range of β_{max} values to which these two methods can be used to calculate the values of k_1 and k_2 was ascertained as follows: the values of k_1 and k_2 were calculated using the methods I and II for β_{max} values ranging from 0.01 to 2.00. Figure 13 shows the difference in k values derived from these two methods at various values of β_{max}. These differences are significantly larger when β_{max} is below 0.40. The magnitude of these differences also depends on the value of t_{max}: the smaller the t_{max}, the larger is the difference in the k values, at $\beta_{max} = 0.40$ and less. The relative error in the values of k of the two methods, $(k_I - k_{II}) \times 100/k_I$, however, is large at these lower values of β_{max} but is independent of t_{max}, as shown in Figure 14.

For β_{max} greater than 1.00, the k values of method I are positive while those of method II are negative and hence meaningless. In pseudo-first-order reactions, β_{max} greater than 1.00 is seldom encountered. Even when β_{max} is greater than 1.00, method I can be used to extract the values of k_1 and k_2 and the kinetic optimization is, therefore, possible. Situations in which β_{max} is greater than 1.00, however, are rare.

Large error associated with the k values for β_{max} below 0.40 seems to be due to a computational limitation in solving equation 11 for κ. For β_{max} in the range of 0.1 to 0.4 the values of κ remain constant, in spite of the use of high precision in solving this exponential function, as shown below:

β_{max}	κ
0.10,000,000,000	0.99,996,948,242
0.20,000,000,000	0.99,996,948,242
0.30,000,000,000	0.99,996,948,242
0.40,000,000,000	0.84,164,428,711

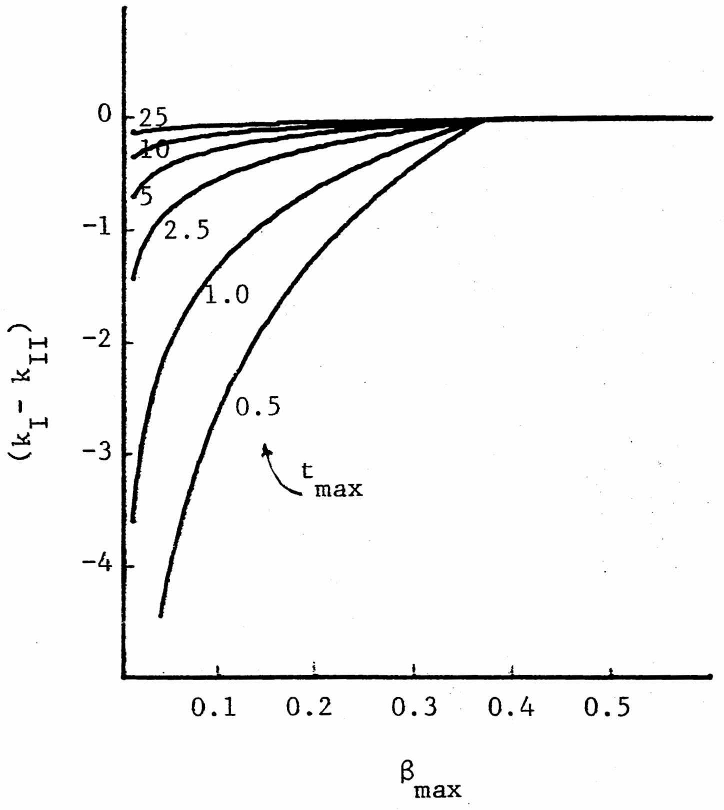


Figure 13. Difference in Rate Proportionality Constants Obtained from Methods I and II Against the Value of β_{max} at Various t_{max}, both for k_1 and k_2

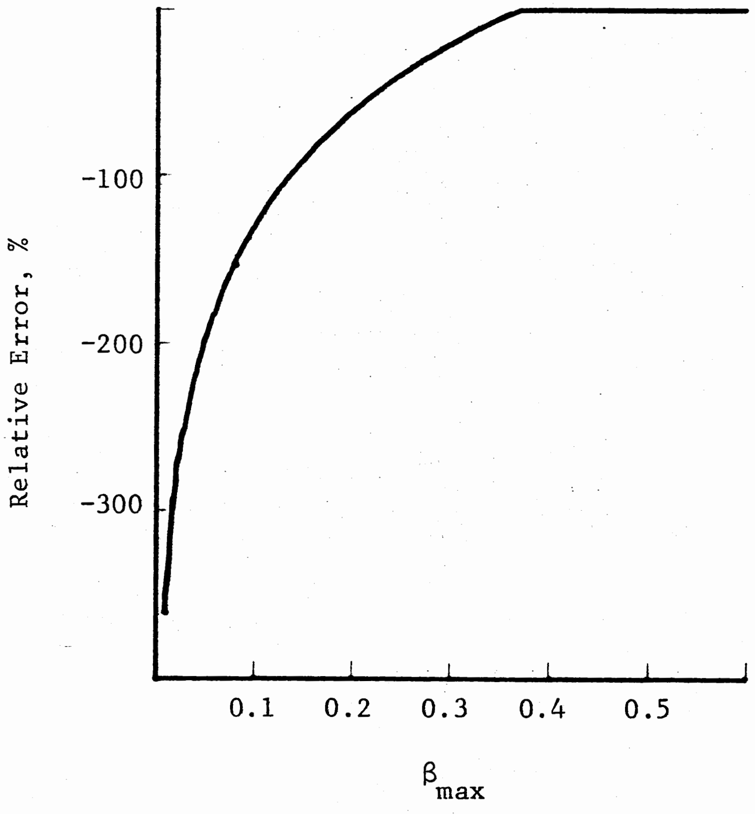


Figure 14. Variation of Relative Error $(k_I - k_{II}) \times 100/k_I$ with β_{max}, both for k_1 and k_2

2

VITA

SAVAKKATTUPALAYAM MUNIAPPAN RAMASAMY

Candidate for the Degree of

Doctor of Philosophy

Thesis: STUDIES IN UNSEGMENTED CONTINUOUS-FLOW ANALYSIS:
Part I. REPETITIVE DETERMINATIONS OF Cu(II) CATALYST
Part II. REPETITIVE DETERMINATIONS OF BROMINE AND CHLORINE IN GASEOUS SAMPLES AT A GAS-SOLID INTERFACE

Major Field: Chemistry

Biographical:

Personal Data: Born in Savakkattupalayam, India, on April 14, 1942 to Mr. and Mrs. S. P. Muniappan; married to Saroja on March 13, 1968; three children: Sumathi, Vimala, and Venkatesh.

Education: Graduated from Board High School, Nambiyur, India, in March, 1959; received Bachelor of Science degree from P. S. G. Arts College, Coimbatore, University of Madras, India, in February, 1964; received Master of Science degree from Pachaiyappa's College, Madras, University of Madras, India, in September, 1966; completed the requirements for the degree of Doctor of Philosophy in Chemistry at Oklahoma State University, Stillwater, Oklahoma, in May, 1981.

Professional Experience: Assistant Professor at P. S. G. Arts College, Coimbatore, India, July, 1966 to August, 1974; Professor and Head of the Department of Chemistry at Gobi Arts College, Gobichettipalayam, India, August, 1974 to August, 1977; Graduate Teaching Associate at Oklahoma State University, Stillwater, August, 1977 to August, 1979; Graduate Research Associate at Oklahoma State University, Stillwater, September, 1979 to date.