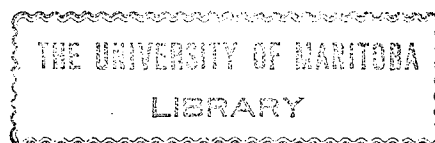


A STUDY OF SELF ABSORPTION IN SOURCES FOR
SPECTROGRAPHIC ANALYSIS

by

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Contents

	Page
Preface	1
Part A	
A Study of Self Absorption in Sources for Spectrographic Analysis.....	3
Part B	
A Direct Reading Microphotometer.....	35
Part C	
Collimated Light Beams in Spectrophotometry..	47
References	61

Preface.

Although much research has been done in the application of spectrography as a tool in industry and scientific investigation, little is known quantitatively of the factors which govern the mechanism of emission from the sources which are commonly used in such work. An understanding of this mechanism would be highly desirable since it would lead to the introduction of more sensitive and more reliable methods of spectrographic determinations. It is known that self absorption plays an important part in determining the relative intensity distribution of the radiation from arcs and flames; information regarding its effect in spark sources appears to be lacking. In Part A a study has been made of intra-spectrum intensity ratio changes caused by variations of self absorption with the changing concentration of the element excited in a condensed A.C. spark source. The spectra of Magnesium, Mercury, and Tin were investigated.

The improvement of quantitative spectrographic methods depends also on the instruments employed in intensity determinations. In Part B a direct reading microphotometer is described which exhibits some new

features of design introduced by G. O. Langstroth and D. R. McRae (7). It combines speed and convenience of operation with minimum fatigue to the operator.

Part C describes an investigation which is of some importance in the allied field of spectrophotometry. The experiments show that errors, due to imperfect collimation, in measured transmission values of solutions may in general be neglected in determinations in which 1% accuracy is sufficient.

The author is indebted to Dr. G. O. Langstroth for suggesting the problems investigated and for his guidance throughout the experimental work involved.

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PART A

A STUDY OF SELF ABSORPTION IN SOURCES FOR
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PART A

A STUDY OF SELF ABSORPTION IN SOURCES FOR SPECTROGRAPHIC ANALYSIS

1. Introduction

In recent years the advantages of spectrographic methods of analysis have been realized more and more, and much work has been done in their development. Present day methods consist of placing the sample to be analyzed in a source and exciting its atoms to radiate their characteristic spectra. The intensity of an appropriate line of the investigated element relative to that of a chosen line of some element (called the internal standard) added in constant amount is determined. Knowing the intensity ratio of these two lines permits the concentration of the investigated element to be read off from a working curve previously determined with known samples under the same conditions of excitation. Various modifications of arcs sparks and flames are used as sources. Common methods of introducing the sample into the source are; drying its solution on an electrode, placing it in an arc cavity, or spraying it into a flame. The assumption made in all such quantitative methods is that the intensity ratio of a line of the unknown element

to a line of the internal standard depends only on the concentration of the unknown. The more nearly this condition is realized, the more reliable and precise is the analysis.

It has long been known that radiation from atoms which has passed through vapour of the same kind of atoms exhibits a spectrum in which the lines show more or less self absorption (9). Since an arc or spark must be considered to be surrounded by a layer of vapour of the electrode material self absorption can be expected in the radiation emitted by these sources. Such an effect is well known in arcs and discharge tubes (8, 11). For example in the determination of the relative intensities of multiplet components (2, 12, 13) special precautions are necessary to minimize the effects of self absorption. This is usually done by decreasing the concentration of the element under investigation until small changes in its concentration have no influence on the intensity ratios (5, 4, 10). It may sometimes be done by adjusting the current in the arc or discharge tube until small changes in current no longer affect the ratios(12). As will be seen later this former criterion cannot always be applied, and when it can, care must be taken to use a sufficiently low concentration of element in the source.

There appears to be no information in the literature

concerning self absorption in spark sources which are commonly used in spectrographic analysis. Although, as pointed out above, some self absorption is to be expected, it is not known whether it has any effect on the spectral line intensities of an element present in the source. Should it have such an effect it may result in different shaped working curves being obtained for different lines of the same element. Furthermore, if the self absorption due to vaporized material about the source is appreciably affected by air currents commonly occurring in the laboratory, it may be a source of serious error in quantitative spectrographic determinations.

With self absorption effects particularly in view a study has been made of the changes in the relative intensities of lines within the spectrum of an element when the concentration of the element in a series of buffered samples was varied over a wide range, all other factors being kept constant. The spectra of MgI, MgII, SnI, and HgI excited in a condensed A. C. spark source have been investigated. A given sample was introduced into the source by drying a measured volume of a solution of known concentration on a plane topped electrode. The concentration of Magnesium was varied over the range 800×10^{-9} to 0.4×10^{-9} grams of Mg/mm² of electrode and that of Mercury and Tin over the range 800×10^{-9} to 8×10^{-9} grams of element/mm² of

electrode.

The results show that marked changes in the intensity ratios of certain lines within the spectra of the elements studied occur when the concentration of the element is varied. With electrode loads as low as 2.7×10^{-9} , 40×10^{-9} , and 8×10^{-9} g/mm² of Mg, of Hg, and of Sn respectively, there is still evidence of self absorption in the resonance lines. At still lower concentrations the self absorption becomes negligible.

The shape of the curves relating intensity ratio to concentration indicates that the usual method of testing for the presence of self absorption in multiplet intensity measurements would lead to erroneous results if the resonance line were involved since, for such lines, there are two regions in which intensity ratio is practically independent of concentration, and the value of the intensity ratio differs markedly in these regions (e. g. fig. 4).

An air current of velocity of the order of 80 cm./sec. directed against the spark proved to be ineffective in changing the self absorption in the spectra of the investigated elements. Increasing the velocity of the air blast to 1500 cm./sec. decreased the self absorption in the Magnesium spectrum slightly, and in the Mercury and

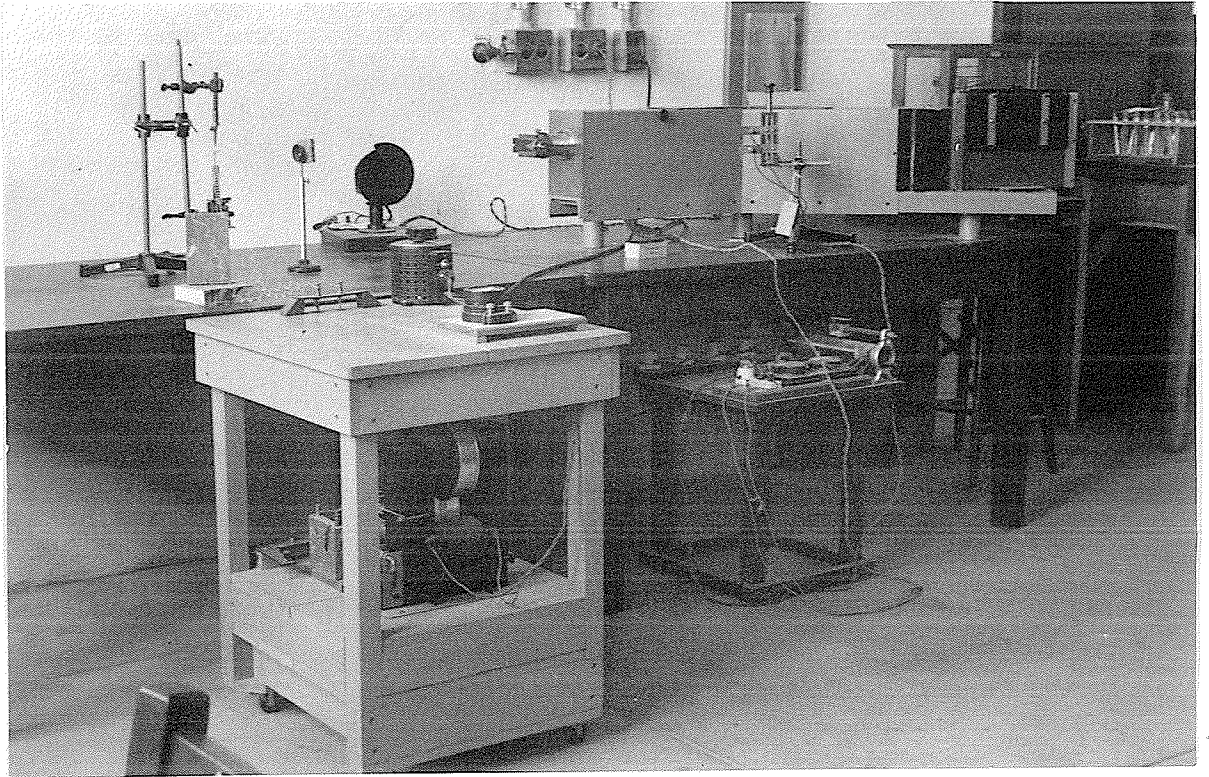


Plate 1.

8

Tin spectra markedly. This leads to the conclusion that air currents ordinarily occurring in the laboratory (much less than 80 cm./sec.) have no appreciable effect on the intensity ratios of spectral lines. It has also been found by K. B. Newbound (M. Sc. Thesis, University of Manitoba, 1941) that there is no indication of any variation of self absorption with extraneous composition of the sample. Hence in spectrographic analysis one can expect no serious troubles due to the variation of self absorption with extraneous conditions.

2. Experimental Procedure

Spectra were recorded with a medium quartz spectrograph, (Plate 1, ~~Figure 1~~.) equivalent to a Hilger E1 or a Bausch and Lomb medium quartz instrument, capable of photographing the full wave length range of the instrument (2000-6000 A) on a single 4 by 10 inch plate. A fairly wide slit (0.006 cm.) was used in the present instance since, for purposes of photometering it was desired to have line images with flat topped density contours.

A condensed A. C. spark source (foreground of Plate 1, ~~Figure 2~~) was used throughout for exciting the atoms in a given sample. The spark holder employed (Plate 2.) is of the point-moving-plane type (1). The spark passes