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MICROANALYSIS BY THE RING OVEN TECHNIQUE

BY HERBERT WEISZ

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CONTENTS

FOREWORD

WHEN I visited the famous Institute for Analytical Chemistry at the Technische Hochschule in Vienna for the first time after World War II, I learned of the original approaches of Dr. Herbert Weisz to the problems of spot test analysis and the chemistry of specific, selective and sensitive reactions.

During my next visit, Dr. Weisz demonstrated to me his first simple model of the ring oven. I recognized immediately that the ring oven technique would fill an important gap in the exploration of spot tests.

During the subsequent years, Dr. Weisz indefatigably pursued a programme of research with the ring oven and published many interesting papers on the subject. The ring oven method which Dr. Weisz created is now recognized all over the world and is used in many fields of analytical chemistry. The potential uses of this method in qualitative and semi-quantitative analysis, radiochemistry, paper chromatography etc. are most promising.

The present state of the ring oven technique demanded the preparation of a monograph on this subject. It is therefore with much personal pleasure that I recommend this first monograph on the ring oven which in my opinion represents an important milestone in spot test analysis.

Rio de Janeiro, June 1959.

PREFACE

THE ever-growing importance of microtechniques in analytical chemistry will, I hope, justify the writing of this monograph. There was a need for a method capable of handling extremely small samples which eight years ago stimulated me to develop the ring oven method. Since then it has been applied and extended by many other chemists. I have been fortunate to be encouraged to continue my work by many colleagues. Therefore my gratitude is due in the first instance to Prof. R. Strebinger, Vienna, Prof. F. Feigl, Rio de Janeiro, and Prof. R. Belcher, Birmingham, the latter who also suggested that I write this monograph.

The editors of this series, Prof. R. Belcher and Prof. L. Gordon, Cleveland, are to be thanked for a number of suggestions which improved the lay-out of the manuscript.

HERBERT WEISZ

Vienna, September 1959.

INTRODUCTION

In qualitative or quantitative analysis, separation of the substances contained in the sample into one or more groups is one of the most important steps. The separation steps must be selected in such a way, that the substances which are collected together in one group do not interfere with the subsequent identification or determination of each substance in the group.

Apart from special techniques, such as distillation or paper chromatography, the methods of analytical separation depend on the conversion of one, or more, parts of the mixture into insoluble compounds which are separated by filtration. This demands a number of chemical operations. The component to be separated must be precipitated by means of a suitable reagent; the precipitate must be filtered and washed; the separated precipitate must be redissolved; and very often it is necessary to concentrate the filtrate as well as the redissolved precipitate.

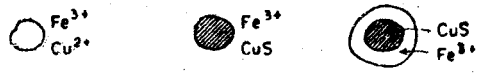
Lack of sufficient test material is frequently a disadvantage especially when many substances have to be detected or determined. It may not always be practicable to dilute the test solution in order to obtain a more easily handled volume, because substances which are present in low concentrations may be diluted to a point where it becomes impossible to identify them.

If only a volume of 1 microlitre (μl) were available, it would be virtually impossible to achieve a separation by one of the usual methods of filtration or centrifugation. It would, however,

be possible to place the drop on filter paper and to add some reagent which would localize one or more components of the mixture as a precipitate on the paper.

The soluble portions, that is, those which are not affected by the reagent, could then be eluted to the outer zone of the paper by means of the capillarity of the filter paper. The procedure can be illustrated by the following example.

A drop of solution contains copper(II) and iron(III) which are to be identified with potassium ferrocyanide. Separation is essential because both ions react with the reagent; either the copper can be fixed with hydrogen sulphide in acidic solution or the iron can be precipitated with ammonium hydroxide. Thus, one of the two metals is fixed on the paper and the unprecipitated component can be washed into the outer zone with a suitable solvent — hydrochloric acid or ammonium hydroxide depending on which precipitant has been used.



At this stage, difficulties begin to arise; for when only a little solvent is used in the washing process, the separation cannot be complete. But when the washing is done thoroughly until, for example, the iron is completely removed from the copper sulphide spot, a large area of irregular shape, in which the iron is very much diluted, is obtained. Despite such difficulties, this method of separation has been widely and successfully used in spot analysis. For example, in the separation of barium and strontium on potassium dichromate paper,[1] strontium chromate is more soluble than the barium salt and therefore migrates into the outer zone of the spot where it can be identified with sodium rhodizonate solution.

However, for this technique to be generally applicable the above difficulties had to be overcome. A method had to be developed by which the unprecipitated portions could be completely removed from a precipitate fixed on filter paper without enlargement of the area of the "secondary" spot and without any decrease in the concentration of the washed-out substances.

This could be achieved by collecting the dissolved components in a previously determined place, where they could again be concentrated. Several simple forms of apparatus have been developed for this purpose and these will be described in the first chapter.

This "Ring Oven Technique" was originally developed as a qualitative separation technique for extremely minute samples, but it has found wide application in different branches of analytical chemistry. Within the past few years, it has been extended to semi-quantitative analysis, to the analysis of radioactive substances, to electrographic analysis, and the like. In the following chapters, the various applications of the ring oven technique are surveyed.

CHAPTER I

THE APPARATUS AND ITS USE

A. THE RING OVEN

THE ring oven *(Ringofen, four annulaire, estufa anular, fornello in forma di annello)*[3] serves the purpose of controlling the washing out of the unprecipitated components from a precipitate fixed on filter paper and of concentrating them again in a previously determined position.

Figure 1 illustrates the ring oven. A cylindrical block of aluminium, 35 mm high and of 55 mm diameter, carries a central bore-hole of 22 mm diameter (dotted lines). A heating wire is installed in this block which is insulated with asbestos. The heating block, *H*, is placed in the base plate, *U*, which also has a 22 mm bore-hole corresponding to that in the heating block. The body is supported on a tripod, *F*.

Gl is a small glass tube, 60 mm long, which is adjustable in height and

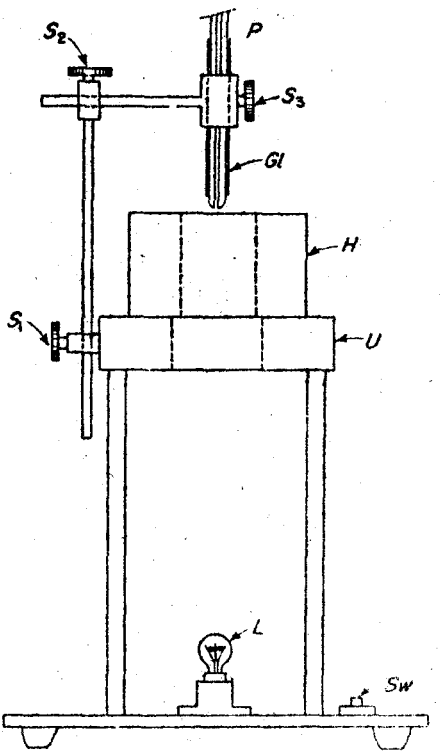


FIG. 1. The ring oven

position by means of three screws, S_1, S_2, and S_3. It serves as a guide tube for the capillary pipette, P, which just fits into it. The guide tube must stand vertically and must point exactly to the middle of the bore-hole, ending a few millimeters above the surface of the block. The pipette and the guide tube are centred by allowing the pipette to drop gently on to a small brass block with a central hole which just fits into the bore-hole of the ring oven, as shown in Fig. 2. A small electric lamp, L, below the heating block allows the edge of the oven to be seen and so enables the elution to be controlled more precisely. Sw is a push-button switch for the electric lamp. The heating wire uses about 20 W at 28 V; an adjustable resistance, or, better, a variable transformer (Variac) can be used to regulate the temperature of the heating block. The surface temperature must be about 105 to 110°C when aqueous solutions are used; in general, it should be a few degrees above the boiling point of the solvent used for washing out. The temperature of the oven remains reasonably constant once the apparatus has been set. A different temperature may be required when organic solvents are used (see the chapter on "Extractions").

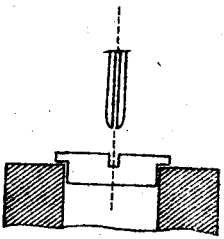


FIG. 2. Centering of the washing-pipette

A type of ring oven which is commercially available is shown in Fig. 3.

The ring oven which is described above is made of aluminium but various other materials can also be used, e. g. copper, stainless steel, gilded copper, etc. For very delicate analyses, plates of platinum or gold can be mounted on the surface of the heating block.

A glass ring oven (Fig. 4) has been described by Balliczo.[3] In this, the hollow glass body, G, which has the same dimensions as the usual metal ring oven, is connected with a condenser on one side and with a 100-ml glass flask on the other side. The flask contains 50 ml of a suitable bath-liquid which has a boiling point about 10°C above the surface temperature desired on the ring oven. When aqueous solutions

are used, a surface temperature of 105 to 110°C is necessary; sym-tetrachloroethylene (b.p. 121°C) is suitable. The bath liquid can be heated with a conventional gas or electric heater.

The Plexiglas ring, *P*, is fixed to the glass body, *G*, by means of three metal screws, *S*. The inner diameter of this ring is exactly the same as that of the filter papers used, 55 mm, so that the paper can always be placed exactly in the same position with the spot centred. Although this is not always necessary, it is advantageous in many cases. The Plexiglas ring also carries the metal holder with the centred glass guide tube for the capillary pipette.

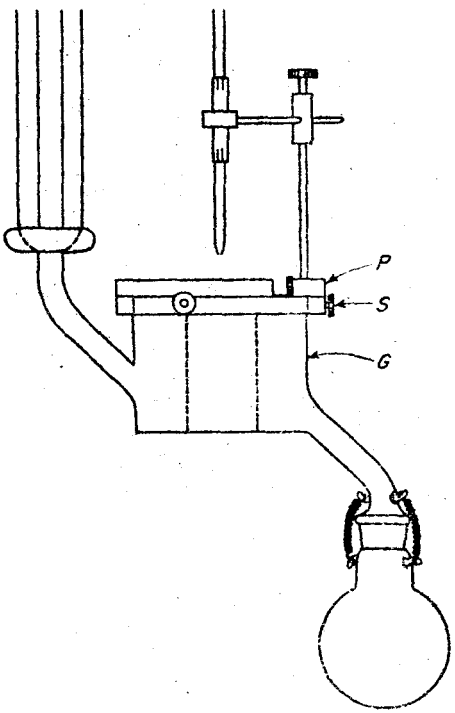


FIG. 4. The glass ring oven

The following example serves to show the mode of operation of the ring oven.

A drop of iron(III) chloride solution (1:10,000 dilution) is placed in the centre of a round filter paper. Only quantitative grade filter paper can be used; Schleicher-Schüll 589[2] and Whatman No. 40 papers have been used for most ring oven work. The filter paper is placed on the hot ring oven so that the spot of solution lies centrally just underneath the guide tube. The filter paper is kept in place by means of a porcelain or glass ring which has an inner diameter of about 25 mm.

All the iron chloride is then washed out with 0.05*N* hydrochloric acid by means of a capillary pipette. This pipette is filled simply by touching it to the surface of the solvent, and is then placed upon the iron chloride spot through the guiding