

ANALYTICAL CHEMISTRY

SOME NEW TECHNIQUES

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ANALYTICAL CHEMISTRY

PREFACE

SEVERAL years ago, the publisher asked me to consider writing a book dealing with the new techniques that had arisen in analytical chemistry. I prepared a list of those techniques which were then undergoing active development and it was at once evident that I could not hope to deal with all of them in the time available. Therefore, I selected eight topics which were of especial interest to myself and reviewed the progress made in these from about 1950 to the end of 1957. In this book, I have not attempted to provide a complete survey of the literature for this period, but have aimed at giving the non-specialist analyst an introduction to these techniques that is as up-to-date as the production of the book would allow. I have endeavoured to define each one in relatively simple terms, to describe any equipment that has been employed and have given, I hope, sufficient examples to show how it has been applied. I have included suitable references to the current literature and made numerous suggestions for further reading.

In writing this book, I have received generous help and encouragement from many people. First, I would like to thank a number of my friends for patiently reading parts of my original draft, making suggestions for its improvement and for correcting any errors. Those who have helped in this way are Mr. L. Brealey, Mr. L. H. Cross, Dr. J. R. Edisbury, Mr. R. Hill, Mr. D. Logie, Mr. J. Muir and Dr. D. E. Palin. I am very grateful for their assistance and must stress that if any errors remain, the fault is mine. Secondly, it is a pleasure to acknowledge the assistance of the following in providing material for the text or in granting permission to reproduce material already published; where such help is not itemized below, a credit line has been inserted at the appropriate point in the text:

The editors of each of the following journals and authors of each of the papers in those journals from which illustrations have been taken:

Analytical Chemistry

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PREFACE

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Beckman Instruments Inc.
British Drug Houses Ltd., for *Tables 1, 2, and 3* on pages 121,
122 and 123

Consolidated Electrodynamics Corporation
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Prentice-Hall Inc.
The Dow Chemical Co., for *Tables 2 and 5* on pages 122
and 125

The Perkin-Elmer Corporation

The Permutit Co., for *Tables 2 and 4* on pages 122 and 124

I also wish to thank Imperial Chemical Industries Ltd., General Chemicals Division, for allowing me to include some unpublished data in the first chapter.

Finally, I am grateful to the publishers for allowing me to use *Figures 8, 9, 12, 13, 19, 20 and 22* (Gas Chromatography) which were taken from one of their own publications and also for their generous help at all stages of the preparation of this book.

‘Calday,’
Church Road,
Huyton.
October 1958

A. G. JONES

CONTENTS

Preface	v
Flame Photometry	1
Differential Spectrophotometry	47
Gas Chromatography	75
The Use of Ion Exchangers in Analytical Chemistry ..	118
Acid-Base Titrations in Non-Aqueous Media	154
Coulometric Titrations	176
Differential Refractometry	196
The Determination of Oxygen and Hydrogen in Metals ..	224
Index	265

FLAME PHOTOMETRY

INTRODUCTION

FLAME photometry is a technique whereby the concentration of a metal in solution may be determined by spraying the solution into a flame and comparing the intensity of the energy emitted which is characteristic of the metal with that of the energy emitted when standard solutions of the metal are similarly treated.

The fact that sodium and several other of the common elements impart characteristic colours to a bunsen flame has been known for very many years. Also the observation that the brightness of the flame varied with the amount of sodium introduced into it must have been observed many times, yet it was only comparatively recently that flame emission has been accepted as the basis of a quantitative analytical method.

Mitchell¹ reported that the earliest flame photometer had been made by Klemperer in 1910 who 'compared visually, in a divided spectroscopy eyepiece, spray-charged oxy-acetylene flames carrying unknown and standard solutions and varied the concentration of the latter until equality was observed'.

The first serious attempt to use flame spectra for quantitative analysis was made by Lundegardh² who used a monochromator, vacuum photocell and amplifier to determine a number of elements with the aid of an air-acetylene flame. Subsequently other workers in the late 1930's and early 1940's attempted to replace the monochromator by optical filters transmitting only narrow regions of the visible spectrum; it will be shown later how this trend has recently been reversed again. In 1945-6, Barnes and his co-workers published two papers in America which were to have a profound effect on the design of flame photometers^{3, 4} while in Europe, Boon⁵ was one of the earliest to describe a simple flame photometer which could be used on a routine basis.

Mavrodineanu⁶ has compiled a bibliography on analytical flame spectroscopy covering the period 1848 to March 1956 which contains 925 entries. An analysis of these references on a time basis is given in *Table 1*.

These figures demonstrate that the period since 1945 has been one of steadily mounting interest in the technique. This has been

FLAME PHOTOMETRY

made possible by the wider availability and increased sensitivity of selenium photocells, the production of good optical filters, particularly of the interference type and the developments in electronic circuits and production of photomultipliers. Many of the analysts using the technique have done so with instruments of their own construction but increasing demands for determinations of the alkali metals encouraged the commercial production of flame photometers, first in America and later in Europe so that by 1955 the

Table 1. An analysis of Mavrodineanu's bibliography on a time basis

<i>Period</i>	<i>No. of references</i>
1848-1930	72
1931-1935	51
1936-1940	82
1941-1945	34
1946-1948	54
1949	34
1950	69
1951	85
1952	100
1953	118
1954	107
1955	97

EEL flame photometer and the Beckman spectrophotometer with a flame photometer attachment were widely used in England and several other English instruments were in production (currency difficulties have prevented the import of the simpler and well-established American instruments). Although spectrophotometers have been used for many years for flame photometry, it is only comparatively recently that any sustained interest has been taken in the possibility of using these instruments for elements other than the alkalis or alkaline earths; *Table 2* (page 6) lists those elements that have been determined together with the spectral lines normally used for measurement. Thus with the increasing use of recording equipment, there is a prospect that more of the classical methods for the determination of metallic elements will be superseded, at least in the larger laboratories.

Because of this divergence of interest, the general principles of flame photometry will be considered first, with special reference to the use of simple instruments, followed by a discussion of flame spectrophotometry.

GENERAL PRINCIPLES

THE GENERAL PRINCIPLES OF FLAME PHOTOMETRY WITH SPECIAL REFERENCE TO THE USE OF SIMPLE INSTRUMENTS

DESCRIPTION AND METHOD OF USE OF A SIMPLE FLAME PHOTOMETER

The lay-out of a typical simple flame photometer is shown in *Figure 1*. With this instrument, air at a given pressure is blown into an atomizer and the suction thereby produced draws a solution of the sample into the atomizer where it joins the air stream as a fine mist

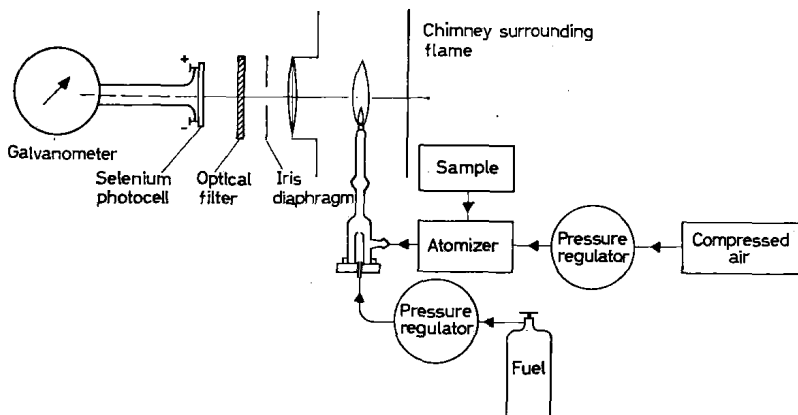


Figure 1. Lay-out of a simple flame photometer

and passes into the burner. Here, in a mixing chamber, the air meets the fuel gas supplied to the burner at a given pressure and the mixture is burnt.

Radiation from the flame passes through a lens, then through an iris diaphragm, which provides a mechanical means of varying the amount of radiation reaching the photocell, and finally through an optical filter which permits only the radiation characteristic of the element to be determined to pass through to the photocell. The output from the photocell is measured on a suitable galvanometer.

The flame is surrounded by a chimney to protect it from draughts. Also, the optical path from the chimney to the photocell is enclosed in a light-tight box or tube to ensure that no extraneous radiation reaches the photocell.

Many instruments of this type have been described. As an example of a flame photometric determination, the method of using one particular model which requires an air-acetylene flame will be described in detail. The model chosen has been built by several workers^{5, 7, 8}; some illustrations of the one built for the writer

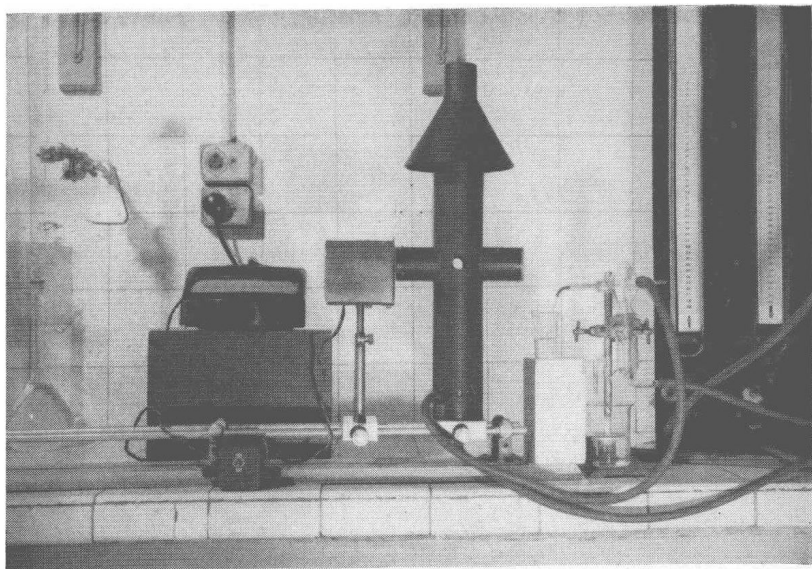


Figure 2. Domingo and Klyne flame photometer—complete assembly (By courtesy, I.C.I. Ltd.)

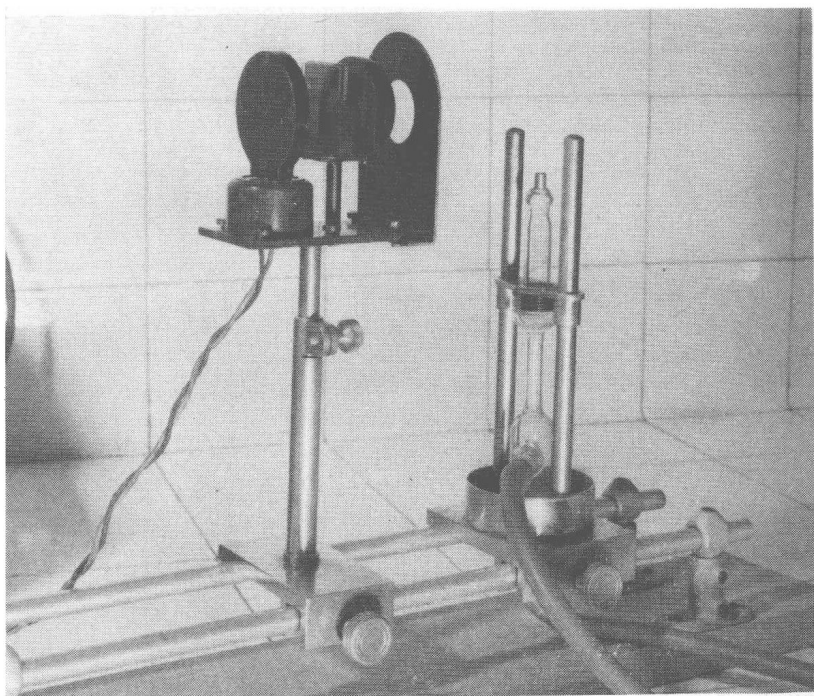


Figure 3. Domingo and Klyne flame photometer—photocell cover and burner chimney removed (By courtesy, I.C.I. Ltd.)

GENERAL PRINCIPLES

(*Figures 2, 3 and 4*) show clearly the details of construction. Although this may be regarded as a poor instrument by present commercial standards, its construction is simple and rugged, maintenance

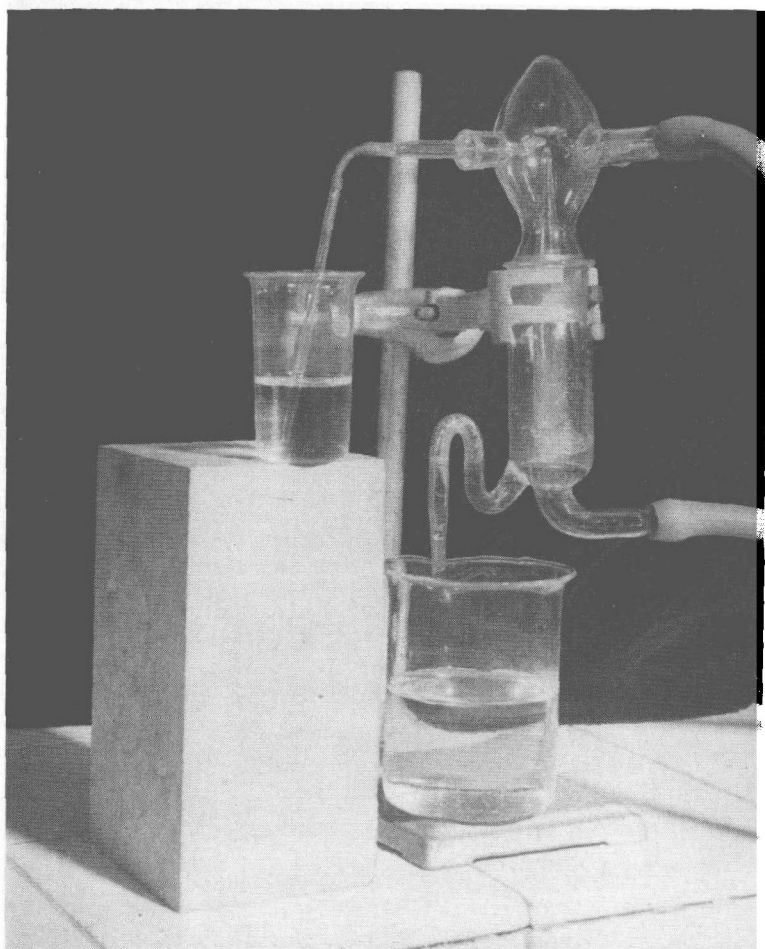


Figure 4. Domingo and Klyne flame photometer—atomizer with sample in position (By courtesy, I.C.I. Ltd.)

presents no difficulty and results obtained with it are adequate for most purposes. It provides a useful example with which to preface the subsequent discussion of the component parts of a flame photometer.

FLAME PHOTOMETRY

It will be seen that the burner and its surrounding chimney are mounted on an optical bench. The iris diaphragm, optical filter and photocell are mounted in a separate housing, also resting on the optical bench. The other components are located to suit the convenience of the operator.

It is preferable that the solution presented to the instrument for examination should be neutral and contain no cations other than

Table 2. Principal lines in flame spectra of elements determined by flame photometry

<i>Element</i>	<i>Wavelength of lines in millimicrons</i>
Barium	553.6
Boron	545* (see also page 40)
Caesium	852.1
<i>Calcium</i>	620*, 554.4*, 422.7
Chromium	427.4
Copper	327.4, 324.7
Gallium	417.2, 403.3
Indium	451.1, 410.2
Iron	372.0
<i>Lithium</i>	670.8
Magnesium	383.0*, 371.0*, 285.2
Manganese	403.1
Nickel	352.4, 341.5
Phosphorus	540
<i>Potassium</i>	766.5, 404.4
Rubidium	780.0
Silver	338.3, 328.1
<i>Sodium</i>	589.6, 589.0, 330.2
<i>Strontium</i>	460.7

* Band spectra are emitted at these wavelengths. Elements printed in italics are those commonly determined with simple flame photometers.

that which is to be determined, e.g. sodium. The steps necessary when this condition is not fulfilled will be discussed later in this chapter.

Before a sample can be examined, the instrument must be made ready for use. The correct optical filter is inserted in the holder, in this case a combination of Chance OY1 and Ilford 803, the iris diaphragm placed in the 'wide open' position and the intake tube of the atomizer is placed in a small beaker of distilled water. The photocell housing is moved away from the chimney which is itself removed from the burner. The air supply is now turned on and adjusted until it is passing into the atomizer at a pressure of about 26 cm mercury; it will be noticed that water is being sprayed into the burner. The acetylene is now turned on and its pressure adjusted

GENERAL PRINCIPLES

until it is close to the working pressure (of the order 50–60 cm water). When acetylene is flowing freely from the burner the flame is lit and the air and acetylene pressures are then adjusted to give a quietly burning flame; these pressures are kept constant throughout the series of determinations in hand. If too little acetylene is reaching the burner when the flame is lit, either from incorrect pressure adjustment or because air has not been completely swept from the acetylene line, the flame will strike back and soot will be deposited in the burner. Should this occur, the burner must be dismantled and cleaned before the work is continued. When the flame is burning quietly, the chimney is replaced on the burner and the photocell housing moved back to its working position. Before proceeding to use the instrument for a determination, the atomizer must be set to give maximum sensitivity. To do this, a solution of sodium chloride is sprayed into the flame (e.g. 20 p.p.m. Na) and the intake jet of the atomizer slowly rotated about its horizontal axis until a position is found which gives a maximum galvanometer deflection. Since the jet is attached to the atomizer through a ground glass joint coated with a heavy grease, it should not move from this setting of its own accord but it is advisable to check this from time to time.

When the instrument is ready for use and sodium-free water is being sprayed into the flame, a small deflection of the galvanometer will be observed. This represents the instrument 'blank' which is a measure of the radiation from the flame passing through the optical filter to the photocell in the absence of sodium. It should be constant for any particular setting of the instrument and, providing this is so, the galvanometer may be re-set to give a zero reading under these conditions.

One further operation is necessary when the instrument is first put into use for a particular determination: an approximate calibration must be carried out for any particular setting of the iris diaphragm. To do this, standard solutions of sodium chloride containing, say, 10, 20 and 30 p.p.m. sodium are sprayed into the flame and the galvanometer readings noted. Although such a calibration will vary from day to day, it provides useful information for subsequent work with samples.

If the concentration of sodium in the sample is unknown, then an arbitrary dilution is made and the resulting solution sprayed into the flame. If the galvanometer deflection is greater than the maximum permissible, the iris diaphragm is slowly closed until the deflection has decreased sufficiently to bring it on the scale, preferably in the range 70–90% of the maximum, or alternatively, the

FLAME PHOTOMETRY

sample solution is progressively diluted to bring about the same result. From a knowledge of the calibration of the instrument at the setting of the iris diaphragm being used, two standard solutions of sodium chloride are prepared such that one (S_1) will give a galvanometer deflection a few divisions below that of the sample and the other (S_2) will give a deflection a few divisions above that of the sample. The three solutions are now examined two or three times in the sequence

S_1 sample S_2 S_1 sample S_2 etc.

The instrument responds immediately to changes in the solution sprayed into the burner and it is not necessary to wash with a water spray between each pair of solutions.

The galvanometer reading is rarely steady, but oscillates slowly over one or two divisions due to fluctuations in the flame emission. Large oscillations occur when the liquid collecting at the base of the atomizer suddenly siphons away to waste. A typical set of readings which might be obtained is as follows, each column to be read downwards in turn:

S_1 (20 p.p.m. sodium)	66	67	73
Sample	65	65	71
S_2 (16 p.p.m. sodium)	57	57	63

The first two columns represent a steady state in the flame but the third column reflects a sudden slight change in flame conditions that caused a change in the level of photocell response. Thus it will be evident that it is advisable to use the mean of several readings in determining the sodium content of a sample. Any large changes in flame output during the course of a series of readings will be quickly spotted and the resultant galvanometer readings rejected.

Assuming that the response of the instrument is linear over the very narrow range of sodium concentrations employed in the examination of a sample, the sodium content of the sample can be readily calculated.

At the end of a series of determinations, water is sprayed into the instrument for a few seconds to remove any sodium from the atomizer and burner. To extinguish the flame it is sufficient with some burners to shut off the acetylene supply. However, with others, it is quite likely that the flame will go out accompanied by a minor explosion and the deposition of soot within the burner, necessitating its being dismantled and cleaned. If, however, at the end of the work, ethyl alcohol is sprayed into the flame for a few seconds instead of water, the acetylene may then be turned off and the flame will die away quietly.

GENERAL PRINCIPLES

Under ideal conditions, the accuracy of results obtained for the determination of sodium with this instrument will be of the order $\pm 3\%$; the accuracy of the determination of other metals will depend upon the intensity of their flame spectra relative to that of sodium. However, conditions are rarely ideal in practice and sample

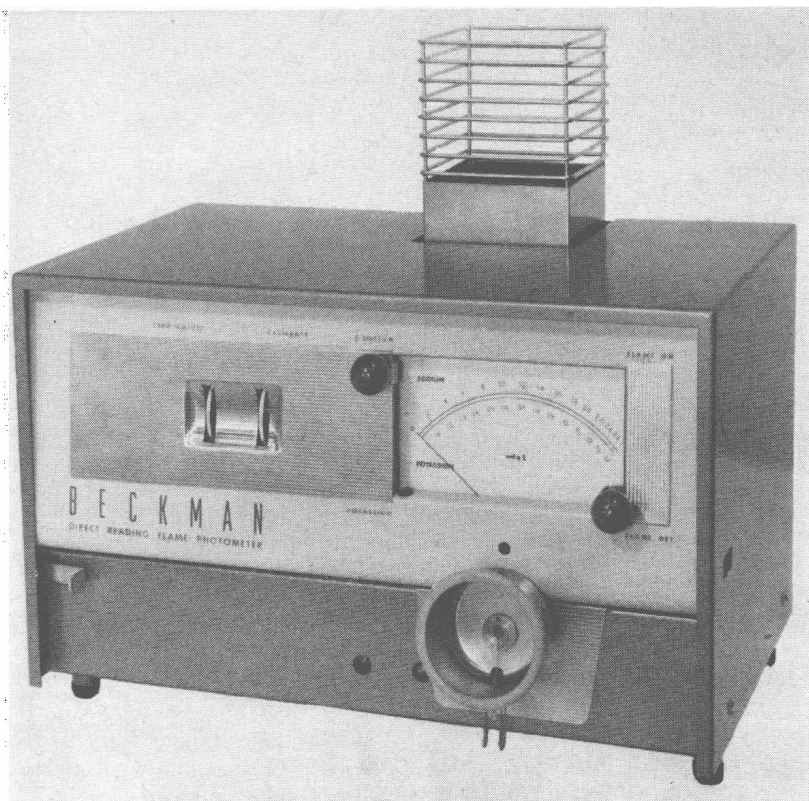


Figure 5. Beckman model 41 direct reading flame photometer (By courtesy, Beckman Instruments Inc.)

solutions often contain substances which can cause inaccurate results unless suitable precautions are taken; such precautions are discussed below.

The method of operating a particular simple flame photometer having been given, attention will now be turned to an examination of the factors which influence the performance of such an instrument and the various changes which can be made in the design or mode of operation.

FLAME PHOTOMETRY

Illustrations of two typical commercial flame photometers are shown in *Figures 5 and 6*.

FACTORS WHICH INFLUENCE THE PERFORMANCE OF A SIMPLE FLAME PHOTOMETER

(1) *The Flame*

The flame consists of a burning mixture of fuel gas and air or oxygen into which the sample solution is introduced in a finely divided state. Acetylene, hydrogen, butane, propane and other

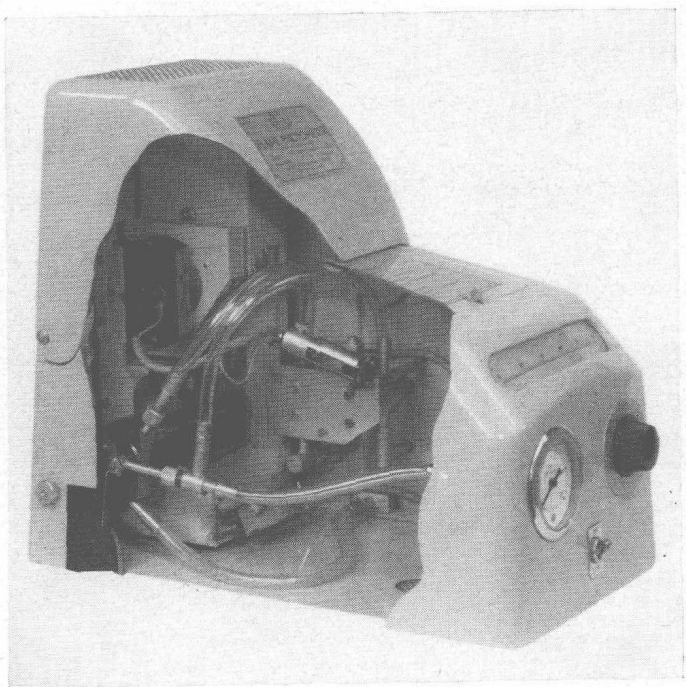


Figure 6. EEL flame photometer (By courtesy, Evans Electroselenium Ltd.)

proprietary gases and town's gas have all been used with success, ready availability often being the deciding factor where a choice has to be made.

The temperature of the flame will, of course, vary with the fuel gas used: the figures in *Table 3*, which are approximations of the data collected by Vallee and Bartholomay,⁹ show the range

FACTORS INFLUENCING PERFORMANCE

available with the commonly used fuels and *Figure 7* shows the temperature variations encountered within two typical flames.

It is only elements which have a low excitation potential that

Table 3. Some flame temperatures

<i>Fuel</i>	<i>With air</i> °C	<i>With oxygen</i> °C
Hydrogen	2100	27-2800
Acetylene	2200	3100
Methane	2000	2700
Ethylene	1900	—
Propane	1900	2800
Manufactured gas	1800	2800

produce flame spectra and the intensity of the flame emission bears some proportional relationship to the flame temperature. As the

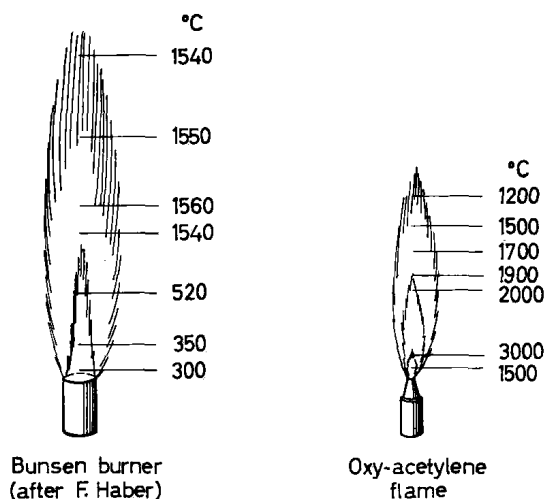


Figure 7. Temperature variation within two typical flames
(Reproduced by permission from *Procedures in Experimental Physics*, by John Strong and others, pp. 513 and 516. Copyright, 1938 by Prentice-Hall, Inc., Englewood Cliffs, New Jersey)

flame temperature is raised, so more elements begin to emit flame radiation and the possibility of interference with a particular determination on a given sample is thereby increased. Thus the emission