Applied Atomic Spectroscopy

Volume 1

Edited by

E. L. Grove

Applied Atomic Spectroscopy

Volume 1

MODERN ANALYTICAL CHEMISTRY

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Preface

From the first appearance of the classic *The Spectrum Analysis* in 1885 to the present the field of emission spectroscopy has been evolving and changing. Over the last 20 to 30 years in particular there has been an explosion of new ideas and developments. Of late, the aura of glamour has supposedly been transferred to other techniques, but, nevertheless, it is estimated that 75% or more of the analyses done by the metal industry are accomplished by emission spectroscopy. Further, the excellent sensitivity of plasma sources has created a demand for this technique in such divergent areas as direct trace element analyses in polluted waters.

Developments in the replication process and advances in the art of producing ruled and holographic gratings as well as improvements in the materials from which these gratings are made have made excellent gratings available at reasonable prices. This availability and the development of plane grating mounts have contributed to the increasing popularity of grating spectrometers as compared with the large prism spectrograph and concave grating mounts. Other areas of progress include new and improved methods for excitation, the use of controlled atmospheres and the extension of spectrometry into the vacuum region, the widespread application of the techniques for analysis of nonmetals in metals, the increasing use of polychrometers with concave or echelle gratings and improved readout systems for better reading of spectrographic plates and more efficient data handling.

Many of the far-reaching and on-going changes in industry and environment control would not have been possible without developments in spectroscopy, and committees of ASTM are continuing their work on evaluation and consolidation of procedures.

The available literature dealing with emission spectroscopy has until now been scattered among myriad sources and we in the field have long recognized an urgent need to gather the new ideas and developments together, in a convenient format. However, the enormous amount of work involved in preparing a comprehensive treatise on the subject has been a deterrent. Finally, this major collaborative effort was undertaken: *Applied Atomic Spectroscopy, Volumes 1* *and 2* have been written by a group of authors, each of whom has an intimate and expert working knowledge of a special area within the discipline. Individual chapters are treatments in depth of new developments, placed within an historical perspective, in many instances incorporating much of the author's own experience.

I wish to extend my special thanks to all the collaborators for their cooperation and patience. The courtesy of the book and journal publishers who gave permission to reproduce figures and tables is gratefully acknowledged, with special thanks to the U.S. Geological Survey.

We also wish to thank the many practicing spectroscopists for their suggestions and help during the editing process, and last, though not least, Mrs. E. L. Grove and Nancy Robinson for editing, typing, and helping to keep detail in order.

E. L. Grove

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Photographic Photometry

1

James W. Anderson

1.1 INTRODUCTION

Photographic photometry is the process of measuring the intensity of radiant energy of specific wavelengths in spectra recorded on a photographic emulsion. Since the formation of a spectrogram takes a finite amount of time, the measurement is more properly the integration of intensity, or exposure.

Photography has played a major role in the development of spectroscopy and spectrochemical analyses. In his studies of the darkening effect of silver chloride by the sun's spectrum, Ritter(1) in 1803 noted that the maximum darkening action was just outside the visible spectrum—hence the discovery of the ultraviolet region. Shortly after the development of the Daguerreotype process in 1839,(2,3) which used sodium thiosulfate as the fixing agent, both Becquerel(4) in 1842 and Draper(5) in 1842 and 1843 obtained photographs of the solar spectrum.

The next important advance in photography was the development by Maddox(2) in 1871 of the dry gelatine plate, which very quickly found widespread use in spectroscopy. Its availability made possible the much improved wavelength measurements and improved catalogs of spectra, typified by Rowland's work(6,7) published in 1887 and 1893. This subsequently led to the wide use of the spectrograph.

Today, photography is one of the four methods for detecting and measuring radiant energy, the other three being photoelectric, visual, and thermoelectric or radiometric. Some characteristics of these four methods are compared in Table 1.1. Wavelength range in the table refers to the spectral region for which the method is useful. Contrast is the general slope of the curve in which the response of the detector is plotted as a function of the quantity of radiant energy, while linearity refers to how closely this plot approaches a straight line.

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Table 1.1 Summary of Methods for the Measurement of Spectral Intensities (Radiant Energy)

Method	Wavelength range (Å)	Contrast	Linearity	Neutrality	Cumulative	Panoramic
Photographic	10–11,000	High	Poor	Poor	Good	Excellent
Photoelectric	10–40,000	High	Good	Poor	Fair	None
Visual	3,900–7,500	High	Very poor	Poor	None	Limited
Thermoelectric	9,000–10^7	Low	Excellent	Excellent	None	None

A detector with high contrast is more sensitive to small changes of signal level but is likely to have a smaller dynamic range or latitude than a detector with low contrast. A detector is said to be highly neutral if the differences in its response to radiant energy of different wavelengths are negligible; that is, it responds in the same manner to the energy of one wavelength as to that of another. Because photographic emulsions have poor neutrality and are also nonlinear in response, they often require different calibrations in different wavelength regions. This is illustrated in Fig. 1.1 as shown by Harrison *et al.*(8) The cumulative property refers to the ability of the receptor to sum up exceedingly low intensities of light by increasing the time of exposure, while the panoramic property means the ability of a photographic emulsion to simultaneously record different wavelengths of radiant energy on different parts of the plate or film.

Pictorial photography is concerned with the linear recording of visually perceived illumination levels of objects under a heterochromatic light, whereas photographic photometry of the spectrum requires precise quantitative comparisons of much fainter and essentially monochromatic beams of radiation. The high sensitivity to small changes of signal level and the cumulative and panoramic properties of the emulsion are important for photometry, but linear recording (which can be realized only over a limited exposure range) is not. Important advantages of photographic photometry include the integration of light from sources of time-varying brightness and production of a permanent record.

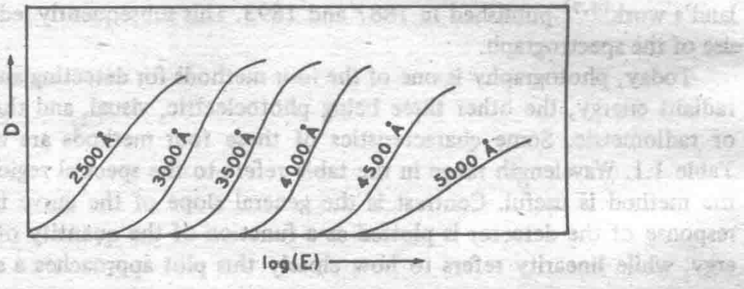

Fig. 1.1 Calibration curves for different wavelengths. The same scale, but different origins, were used to prevent overlap. (From Harrison *et al.*(8))

1.2 THE PHOTOGRAPHIC EMULSION

The photographic emulsion is a thin layer of gelatin containing a suspension of very fine, light-sensitive silver halide crystals or grains. While the gelatin is in the liquid state, it is coated on glass or on cellulose acetate or polyester base and allowed to dry.* Glass plates have an advantage with respect to dimensional stability but are restricted to spectrographs with flat or moderately curved focal planes. With standard plate widths of 2 and 4 in., they also provide more area for accepting a greater number of spectrograms, which permits more latitude in including exposures of standard samples for direct comparison to unknown samples. Although film is subject to expansion and contraction and presents some mechanical problems in processing and in being held flat in microphotometers, it can readily be bent to steeply curved focal planes. Film also avoids the obvious breakage damage to which glass is subject. In general, the emulsion layer on glass plates is slightly thicker than on film, which tends to make them more sensitive. On the other hand, the emulsions on film products have a thin clear gelatin overcoat of about 1 μm for protection against abrasion and handling. Kodak$^{(9)}$ specifically recommends that the emulsion surface of plates are not to be wiped, because they are very soft when wet.

The light-sensitive material is a mixture of silver bromide with some silver iodide and traces of nucleating compounds. The size of these crystals or grains is carefully controlled within narrow limits because many properties of an emulsion are grain-size-dependent. The average grain size may vary from about 5 μm in diameter for fast emulsions to submicroscopic for the slow Lippman emulsions. In general, the larger the average grain size, the more sensitive the film (partly because larger grains intercept more of the incident energy per grain) and the lower the contrast of the emulsion. The converse is also true, and thus one can expect that a fine-grained emulsion is generally slow with high contrast. This natural association of emulsion characteristics is unfortunate because the most desirable emulsion should have the finest grain possible to provide sharp resolution and yet be fast at the same time.

Another characteristic of an emulsion is the dynamic range over which it responds to radiation. The logarithm of the useful dynamic range or *latitude* varies inversely with the *contrast* or gamma of the emulsion. Both latitude and contrast also depend upon the minimum number of quanta a grain must absorb before it becomes developable and upon the dispersion of grain sizes about the average grain size of the emulsion. This is illustrated in Fig. 1.2, in which curve 2 represents a low-speed emulsion with high contrast, short latitude, and relatively poor sensitivity.

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*In some special emulsions, more than one such coating may be applied. If two or more coatings are applied, they usually differ in grain size and sensitivity. The purpose of this procedure is to extend the dynamic range for visual photography.

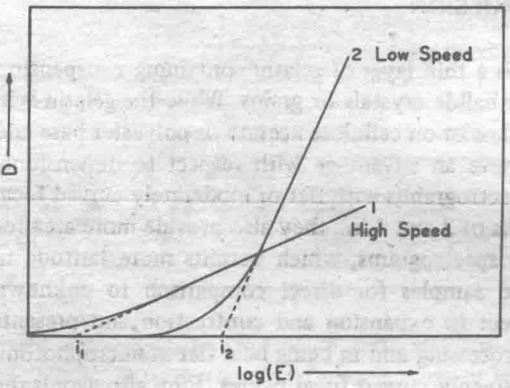

Fig. 1.2 Characteristic curves for typical emulsions with high and low speeds. (From Harrison *et al.*(10))

Speed, contrast, and latitude are all functions of wavelength. Both the absorbance of the photosensitive layer and the number of quanta that a grain must absorb before it can be developed depend upon wavelength. The absorbance of the photosensitive layer is by the gelatin substrate as well as by the silver halide grains embedded in the substrate. The absorption by gelatin, which begins below 2500 Å, affects the contrast of the emulsion, while the absorption by silver halide affects both sensitivity and contrast. These effects can be modified by various sensitizing dyes which are added to the emulsion to improve response at wavelengths above 5000 Å, where the silver halide itself is transparent. Gradient is a measurement of contrast in terms of the slope of the straight line between two specified densities on a characteristic curve. Eastman Kodak has described typical variations in gradients for different emulsions in which they

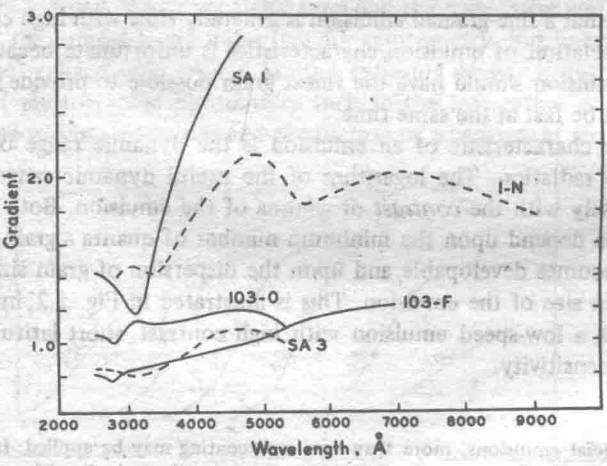

Fig. 1.3 Approximate gradient–wavelength curves for some typical spectrographic (plates) emulsions.