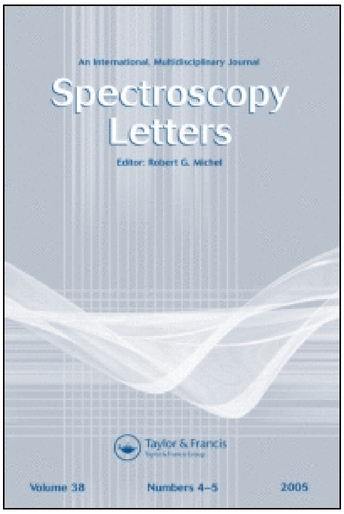

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Flame Photometry and Atomic Absorption Spectroscopy

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FLAME PHOTOMETRY AND ATOMIC ABSORPTION SPECTROSCOPY

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In the past few years the applications of atomic absorption spectroscopy have mushroomed to prodigious proportions.

Its popularity is at an all time high and it is rapidly becoming almost a requirement in all self respecting analytical laboratories.

However, in the midst of this phenomenon one or two voices have been raised in protest. From the lectern they have insisted that the gullable public be protected from the claims of the developers of this new field and if possible they should be encouraged to return to using flame photometry.

Perhaps it is time to survey these fields in the quiet of the research laboratory rather than the presentation room where the debate is short and seldom complete.

In evaluating analytical fields it is most important to be unemotional about the topics. No one gains if the evaluator feels he must defend 'his' field. To do so violates the first commandment of research. "Thou shalt not get emotionally involved with the atoms or molecules."

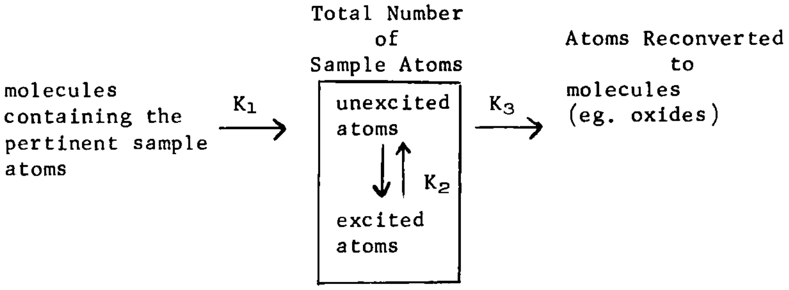
The present enthusiasm for atomic absorption has been termed a fad. This may be a fair reflection of the status, but we should define 'fad' in order to agree or disagree.

At irregular intervals new analytical fields evolve. They may enjoy periods of extreme popularity and then take their place amongst the other disciplines of analytical chemistry. Good examples of fads of the past are infra-red, gas chromatography and mass spectrometry. Their popularity stems from the fact that they are able to provide information which was not previously easily available. They pushed back an availability barrier. A fad was developed based on the desire to obtain and use the new information.

It should be remembered that the people who buy the equipment use money obtained from somebodies budget. Justification is necessary and it is not enough to say "So-and-So said this technique is great", or "Everyone has one, we should have one too". Mini-skirts and long hair are fads, but scientific fads are not based on such guide lines.

It has been said that the early workers in the field of atomic absorption made wild and unjustifiable claims. The most contested claims are those in the areas of interferences. I myself have stated that atomic absorption enjoys an inherent advantage over flame photometry, because it involves the number of unexcited atoms rather than the excited atoms. The basis for the claim is as follows:

The atom population in a flame is in a state of dynamic equilibrium which can be depicted in the following simplified form.



The total number of atoms depends on the efficiency of their production (i.e., K_1) and their rate of loss (K_3). The number of excited atoms is such a small percentage of the total atom population that in most cases it can be ignored. Hence, the atomic absorption signal is predominantly controlled by K_1 and K_3.

However, in the case of flame photometry it is the number of excited atoms that is measured, and this is very dependent on K_2. Hence, the signal measured in flame photometry is a function of K_1, K_2 and K_3. Extra experimental control is necessary to minimise the effect of K_2 which is affected by temperature, chemiluminescence, etc. This can be done in practice, but every extra control is a potential source of error and flame photometry finds itself at an inherent disadvantage.

Any factor which affects the total atom population will affect flame photometry and atomic absorption more or less equally. But any factor which affects the equilibrium between ground state and excited state atoms usually affects the emission signal much more than the absorption signal.

It has been claimed that there are no radiation interferences in atomic absorption. This is an over statement. However, in the sense that two elements do not absorb at the same wavelength; this statement is virtually, but not completely, true.

It has also been observed that the products of combustion from the solvents and the flames themselves absorb at various wavelengths, particularly the shorter wavelengths. Their absorption may add to the atomic absorption signal. This of course is also a type of radiation interference and is a source of error. However, to equate these interferences with the radiation interferences experienced from the oxides of metal impurities and other emitting species in a flame is not realistic. This source of error has been a major problem in flame photometry for many years. Decreasing the spectral slit width decreases the problem but does not eliminate it. Correction for background changes may be made and this goes far to solving the problem. Unfortunately this is not always easy to do. The error may not be significant when samples of pure compounds are being investigated. However, it becomes very important when an industrial operator brings into the laboratory a sample for analysis. Frequently he does not know the concentration of the impurities (so a correction cannot be made) or even what impurities are present. In fact he may be seeking that very point of information.

Reduction to practice classified many hitherto theoretical problems. In practice, flame photometry is more susceptible to radiation interferences than atomic absorption.

It has been stated that the instrument companies have oversold the field. In a sense this is true of all instrumental methods of analysis. The instrument companies are frequently able to achieve better operating performances from their equipment in their research laboratories under their ideal conditions than the analyst in the field is able to achieve. Frequently the instrument manufacturer has better trained personnel at his disposal. Often they are experts in their field. This is seldom true in the industrial analytical laboratory. However, it is unrealistic to suggest or even infer that the instrument companies deliberately try to deceive their customers.

The manufacturer knows that deception is the road to ruin. A customer will not remain deceived for long because he will use the equipment and then evaluate it himself. One sale based on deception may be possible, but never two sales. The analyst who justified the purchase of the equipment, but then finds he cannot back up his justification, will not allow himself to be embarrassed twice.

However, there is usually a gap between the performance claimed by the manufacturer and that achieved by the analyst. We have grown accustomed to this in all fields, but it is no worse in atomic absorption than any other field.

It has been claimed that the detection limits obtained by some well known workers in flame photometry are superior to those reported in the literature for atomic absorption. These data may be quite valid. However, when we define sensitivity in terms of signal to noise level, we are really comparing the high performance of that research worker's equipment, operating under ideal conditions, with conventional equipment. It would be interesting to see the sensitivities achieved by the same worker using commercial equipment in an industrial laboratory. It should also be remembered that industrial laboratories seldom have such highly trained personnel to run their samples and cannot expect to achieve these sensitivity limits.

It must also be pointed out that the claims and counter claims concerning interferences in atomic absorption relate to the accuracy and precision of the method. Detection limits are almost irrelevant to this question and cannot be used as proof of interferences or lack of interferences.

It has been said that in flame photometry several elements can be analysed consecutively merely by changing the wavelength setting of the instrument. This points out one of the major disadvantages in atomic absorption where the hollow cathode must also be changed to analyse a different element. Some progress has been made in reducing the problem by using multi-element hollow cathodes or turret holders. However, this is an inherent advantage that flame photometry holds in its favor.

In summary flame photometry has equal or better detection limits for some elements; atomic absorption has equal or better sensitivity for other elements. Flame photometry can give good precision and accuracy under very carefully controlled conditions. But the average industrial laboratory using commercial equipment and the 'average' analytical chemist can expect to get more reliable quantitative results using atomic absorption on a day-to-day basis.

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