

Photoelectric measurement of flame temperatures by line reversal

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In flame photometry the calibration curves and the mutual interference effects of the elements largely depend on the temperature. Consequently, when we investigate the properties and peculiarities of flame photometers, measurements have to be made of the temperature as a function of time, height above the burner, composition of the gas mixture, etc.

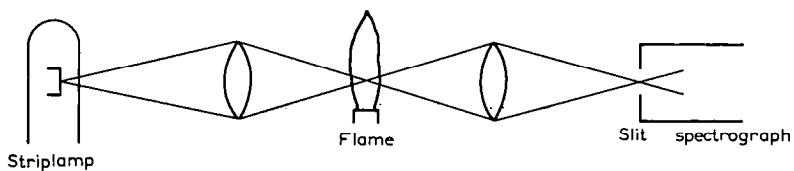


Fig. 1. Principle of temperature measurement by line reversal.

In order to measure these temperatures under varying conditions we have set up an apparatus which is a photoelectric modification of the well-known method of line reversal. This method is illustrated by Fig. 1. A tungsten-ribbon lamp is imaged in the flame which contains vapour of some metal, e.g. sodium. The flame and the image of the ribbon are imaged together on the slit of a spectrograph. In

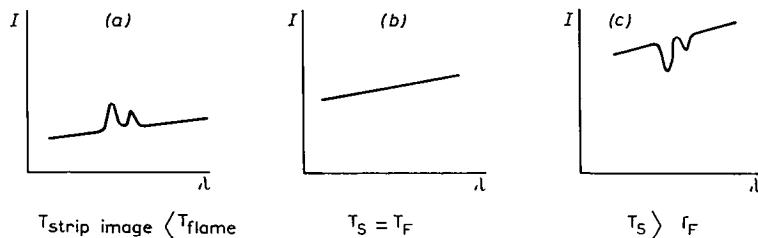


Fig. 2. Spectral intensity as a function of wavelength, for three different values of the brightness of the strip image (schematically).

the vicinity of the yellow sodium lines the spectrum will show an intensity profile as drawn in Fig. 2. The sodium lines appear as emission lines when the brightness temperature of the filament image in the flame is lower than the flame temperature (Fig. 2a), and as absorption lines when the temperature of the image is higher (Fig. 2c). At an intermediate temperature the lines are not distinguishable from the continuum (Fig. 2b); then the temperature of flame and filament image equal each other. The brightness temperature of the ribbon image can be found from the brightness temperature of the tungsten ribbon by taking into account the reflexion losses at the glass bulb and at the lenses.

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With visible lines, visual adjustment to disappearance of the lines is easy and this method is often used. However, in routine measurements it becomes fatiguing and it fails in the ultra-violet. Photographic observation is still possible then—one takes a series of spectrograms at different strip brightness temperatures and finds the correct temperature by interpolation—but it is time-consuming. In both cases, especially in the latter, the photoelectric method is preferable in the long run. Following a suggestion of Dr. ALKEMADE we have arranged the photoelectric measurement as follows (Fig. 3):

The sodium lines F obtained in a prism spectrograph with autocollimation are imaged enlarged on a narrow exit slit S by means of an additional lens L . Near this lens is a small mirror M mounted on the coil of a moving-coil milliammeter. The

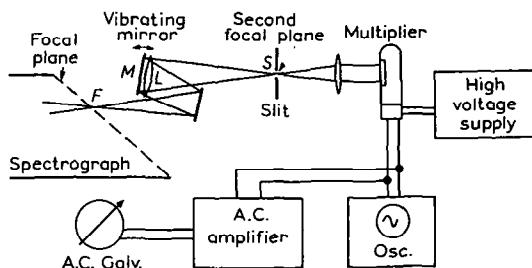


Fig. 3. Diagram of the photoelectric arrangement for line reversal measurements.

yellow light is reflected by the mirror and when the milliammeter is fed with an alternating current, the vertical spectral lines vibrate horizontally across the vertical exit slit. The amplitude of the vibrations is controlled by the current, which has a frequency of 25 c/s. The lines cross the slit 25 times per second in either direction, giving a 50 c/s light signal to the photomultiplier, an RCA 1P28. The multiplier is connected to an oscilloscope as well as to a 50 c/s a.c. galvanometer.

The oscilloscope screen will show the intensity profile of the lines (Fig. 4), broadened, of course, by the spectrograph and by the exit slit. The part of the spectrum which is observed decreases with the amplitude of the mirror vibrations until, finally, only light from one component of the doublet is intermittently passing through the exit slit. The pictures of Fig. 4 were made with only the flame burning and not the strip lamp. When the current through the strip lamp is increased, the lines vanish but the photocurrent noise, which is caused by the continuous spectrum and which is visible on the screen, is large and impedes a correct current adjustment. It is therefore preferable to use the a.c. galvanometer or some other synchronous rectifier. The galvanometer responds well to the 50 c/s light signal, but the visible noise is much less because of the small bandwidth, which is only 1 c/s, and because the apparatus is phase sensitive. The galvanometer deflection is proportional to the difference in intensity between line and adjacent continuum, so that at the reversal point the deflection will be zero. It should be noted that the variation of intensity with wavelength in the continuum does not give a deflection, for this variation produces mostly a 25 c/s signal, which is not detected.

In our preliminary measurements [1] we plotted the galvanometer deflection against the intensity of the continuous spectrum. The intersection of the straight line, thus found, and the line of zero deflection is the reversal point. The slope of the graph and hence the random error in the position of the intersection are dependent on the sodium concentration. With moderate concentrations this error amounts to about 2% of the continuum intensity or 5° centigrade. It is in fair agreement with the computed statistical variation of the number of electrons released per second at the multiplier cathode.

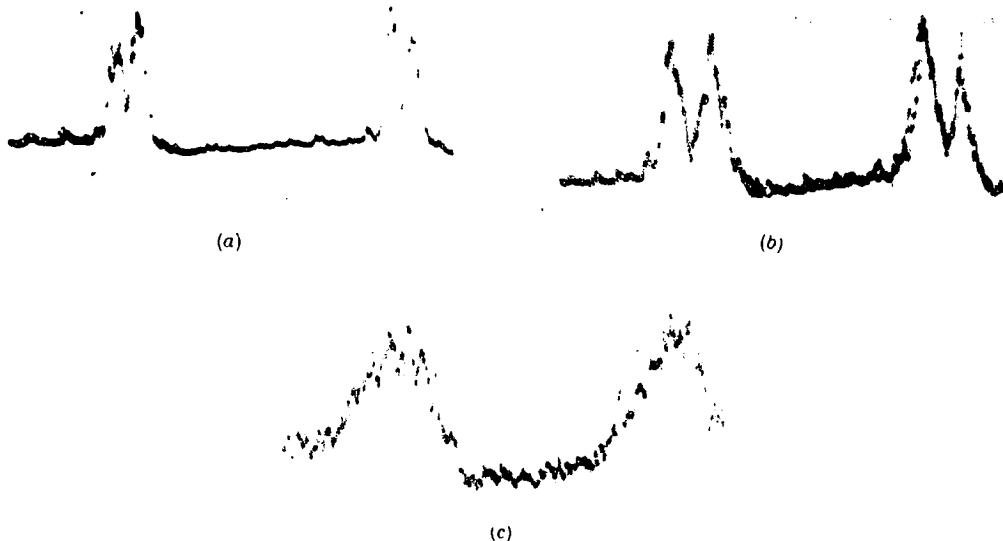


Fig. 4. Photographs of the oscilloscope screen: *a* Doublet and adjacent wavelength region, *b* doublet (smaller amplitude of the mirror vibration), *c* one component (very small amplitude). The figure shows also the opposite line profiles, corresponding to the opposite motion of the mirror.

At first we used an ordinary (cylindrical) flame from a burner with a grid, fed by acetylene and air. The measured temperature appeared to be dependent on the sodium concentration in the sprayed solution. This unwelcome effect is due to light absorption in the cooler outer zone of the flame (self-reversal of the spectral lines). The maximum temperature drop, measured when the highest concentration was used, amounted to 75°C. To check the explanation we surrounded the flame with another flame of the same gas composition, which was independently fed and in which no sodium was vaporized. Thus we came to use a broad flame of which only the central part was coloured. The result of our measurements on both flames are presented in Fig. 5. The measured temperature of the ordinary flame appears to drop with increasing sodium concentration, while that of the broad flame is independent of the concentration within the experimental errors.

To attain the maximum temperature we varied the fuel gas to air ratio. The maximum was reached with an overdose of 15% of air as compared to stoichiometry.

The foregoing measurements were made at a height of about 10 mm above the

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blue cones. One might expect a gradual drop in temperature with increasing height because of sideward energy losses. But in measuring the dependence of the temperature on the height we found a noticeable increase in a range of a few centimetres. The temperature maximum in our case occurred at 18 mm above the blue cones. This initial increase may be explained by a lag in excitation of the sodium atoms.

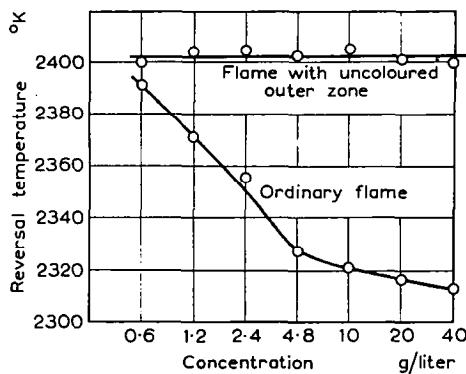


Fig. 5. Measured reversal temperature as a function of NaCl concentration in the sprayed solution.

The chemical energy is transformed into kinetic energy and excitation energy of the molecules taking part in the combustion, and it takes some time before the energy is equally divided between all the particles in the flame. Apparently this equilibrium was not reached under 2 cm from the combustion zones. The rise velocity of the gas mixture was 2.5 m/sec (Fig. 6).

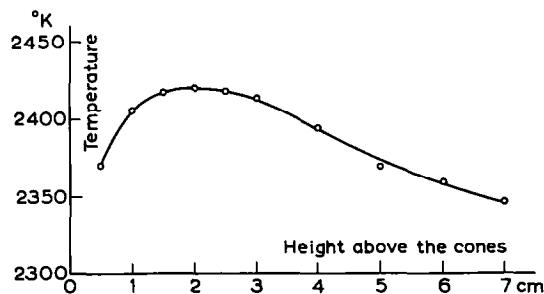


Fig. 6. Temperature as a function of height in the flame.

There are many other factors influencing the flame temperature which are to be investigated yet, for example, heat losses to the burner. Partly this energy returns to the flame by the preheating of the gases in the burner. As a result, the given temperatures are still somewhat dependent on the type of burner. With the burner used this preheating amounts to at least 90°C. Further, the influence of moisture, aceton content of the acetylene gas, gas velocity, etc. have to be checked.

A systematic error of the method was recently investigated in our institute [2]. It arises from the fact that in the flame there is no radiation equilibrium: more

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light is emitted than is absorbed from the surroundings. This leads to a slight decrease of the population of the upper level of the sodium line, equivalent to a temperature difference of 8° at most. We therefore measure an excitation temperature which is correspondingly lower than the actual gas temperature.

References

- [1] SNELLEMAN W. and SMIT J. A. *Physica* 1955 **21** 946.
- [2] BOERS A. L., ALKEMADE C. T. J., and SMIT J. A. *Physica* 1956 **22** 358.

Discussion

Dr. VAIDYA: What is the effect of size of NaCl particles?

Answer: The NaCl was introduced into the flame by spraying a solution. The drops were small, so that they will have evaporated before reaching the part of the flame where the temperature has been measured. We do not expect NaCl particles in this region.

Herr EICHHOFF: Wird bei dieser Methode tatsächlich die "Flammen"-Temperatur gemessen, oder ist der bestimmte Temperaturwert abhängig davon, welche Linien und welche Elemente benutzt werden, da ein Temperaturstrahler mit einer Emission angeregter Atome auf verschiedenen Teilen der Planck'schen Strahlungskurve verglichen wird?

Antwort: Unabhängig von der Wellenlänge gilt, dass, wenn die wirkliche Flammtemperatur und die "Strahlungs" Temperatur des Bandlampbildes übereinstimmen, die Absorbtion gleich gross ist wie die Emission and also das "Umkehrpunkt" realisiert ist. Die "Planck'sche" Abhängigkeit ist verarbeitet in die Berechnung der Temperatur des Bandlampbildes.

Mr. SUGDEN: a. Have other metals than sodium been used, and if so, how do the results compare with those for sodium? b. Have you considered the recombination of excess-radicals as a possible reason for temperature increases in the lower part of the gases?

Answer: a. No other metal than sodium has yet been used. b. This has not been considered. (Up to now these "chemical" problems were beyond the scope of our investigation.)

Herr Prof. FISCHER: Beantworten Ihre Messungen nicht die Frage von Herrn van Calker, welchen Einfluss wechselnde Mengen von Substanz (0,4–4,0 g/l) auf die Flammtemperatur ausüben? Wenn ich recht verstanden habe, ist kein wesentlicher Einfluss vorhanden. Dies hat aber nichts zu tun mit dem Einfluss des Gas-Sauerstoff-Mischungverhältnisses, der bekanntlich sehr gross ist.

Antwort: Dass ist richtig.