

Emission Spectra of Molecules Observed During Carbon Furnace Atomisation

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Molecular-emission spectra from CN and C₂ radicals and from molecules formed during the atomisation of solutions of calcium, strontium and magnesium in carbon furnace atomisers are described. Spectra from metallic species are compared with analogous spectra observed by other workers in flames and arcs and are shown to be more closely related to the spectra of the oxide rather than hydroxide species of these elements.

Keywords: *Molecular-emission spectra; carbon furnace atomisation; CN radicals; C₂ radicals; alkaline earth metals*

In several recent publications,¹⁻⁴ useful detection limits have been reported for a wide range of elements by the measurement of atomic-emission signals during carbon furnace atomisation. The background radiation in this technique consists of a continuum, which is black body in nature,^{3,5} and molecular band emissions from species such as CN (particularly strong when nitrogen is used as purge gas) and C₂.⁶ Careful optical baffling can be used to eliminate the direct measurement of tube-wall radiation, and the continuum is then caused only by Rayleigh scattering of this tube-wall radiation by the constituents of the vapour phase.⁵ Wavelength modulation background correction can be used to subtract the continuous background signal and the analytical system then becomes limited by the shot noise at the photomultiplier rather than the signal to background ratio.³

In emission spectrometry, spectral interferences can arise from other atomic or molecular species that emit radiation within the band pass of the monochromator at the analyte wavelength. A study of spectral interferences between atomic species during carbon furnace atomisation has been carried out⁷ and will be reported elsewhere. This study suggested that such interferences would be less significant than in other emission techniques. Many workers have reported measurements of molecules in the carbon furnace using absorption techniques and the occurrence of molecular absorption is one of the reasons for the necessity of using background correction in carbon furnace atomic-absorption spectrometry. Apart from early studies by King (described by Gaydon⁸) who operated the carbon furnace in an air atmosphere, no molecular-emission spectra have been reported from analytes in carbon furnace atomisation. During the development of a carbon furnace atomic-emission procedure for the determination of barium in the presence of large amounts of calcium, background emission from the calcium matrix was observed at the 553.5-nm barium line.⁹ This emission was caused by a molecular species formed from calcium.

Emissions by metal oxide and hydroxide molecules have been well characterised in flames and arcs.^{10,11} In carbon furnace atomisation the relative concentration of hydroxide species would be expected to be much lower than in flames owing to the low concentration of water molecules in the inert atmosphere. The solvent water present in aqueous samples is removed during the initial drying stage of the atomisation procedure. The intermediate species in most proposed mechanisms of atom formation in furnace atomic absorption is the metal oxide.^{12,13} It might thus be expected that emission from molecular species during carbon furnace atomisation would be largely due to oxide species. Such emissions can cause spectral interference in a number of specific analytical applications. The molecular-emission spectra observed to date are described in this paper and are compared with analogous flame emission spectra.

Experimental

Reagents

Reagents of the highest available purity were used throughout. De-ionised water was used in the preparation of all solutions.

Stock solutions of each element were prepared by dissolving the appropriate amount of salt (either nitrate or carbonate) in de-ionised water, with addition of a sufficient amount of nitric acid to give a final acid concentration of 10^{-2} M. Stock solutions were diluted with de-ionised water as required.

Apparatus

Four different instruments were used in this investigation. An HGA-72 heated graphite atomiser was used mounted in a Perkin-Elmer 306 atomic-absorption/emission spectrometer. The use of this instrument in carbon furnace atomic-emission spectrometry has been described elsewhere^{1,4} and it was used in an analogous procedure for molecular-emission measurements. Emission measurements were taken point by point at selected wavelength intervals, each point being measured during a separate atomisation sequence. At each wavelength, the continuum background emission was measured and subtracted. The spectral band pass was nominally 0.4 nm. Molecular-absorption spectra were also obtained in an analogous manner using a Hitachi 390 tungsten-filament lamp as a source.

An HGA-74 heated graphite atomiser was mounted in front of a Hilger and Watts Monospek 1000 monochromator. This is a 1.0-m Czerny-Turner monochromator and an EMI 9592B photomultiplier tube was used as the detector. The spectral band pass was 0.4 nm. The focusing of emission from the centre of the graphite tube into this monochromator and the conditions of measurement have been described previously.⁵ Molecular spectra were again obtained by a point by point technique as described above.

An HGA-2100 graphite furnace was mounted in front of a PAR optical multi-channel analyser which consisted of a 1208 spectrometer (a modified 0.25-m Jarrell-Ash Ebert monochromator) coupled to a 1205D silicon intensified target detector and a 1205A console control centre. The output from the vidicon detector was displayed on a Tektronix 585A oscilloscope and the spectra were recorded with a Polaroid camera. The spectrometer had a grating with 590 grooves mm^{-1} and a blaze wavelength of 300 nm. The coverage of a single spectrum was 70 nm and was sufficient for the bands under investigation. The instrument had 500 channels over 70 nm, giving a resolution of 0.14 nm per channel. Emission measurements were made in a 3-s time window during the atomisation stage of the HGA-2100.

In the final system, the HGA-2100 graphite furnace was mounted in front of a 0.5- or a 0.25-m Ebert monochromator equipped for wavelength modulation.³ Using the 0.5-m monochromator a spectral range of about 1.0 nm was continuously scanned by a vibrating quartz refractor plate in the optical beam of the monochromator. Using the 0.25-m monochromator, a spectral range of about 10 nm was continuously scanned by an oscillating mirror mounted at the exit slit of the monochromator. The photodetector signal was directed to the vertical input of an oscilloscope, while the horizontal input was connected to the source of the modulation waveform. The system, which has been described previously,¹⁴ provides a real-time spectral intensity scan over a limited wavelength range on the oscilloscope screen.

The carbon furnaces were operated under the conditions shown in Table I.

TABLE I

OPERATING CONDITIONS FOR CARBON FURNACES

Fifty-microlitre aliquots of solution at appropriate concentrations were used in all instances.

Furnace	HGA-72	HGA-74	HGA-2100
Drying temperature/ $^{\circ}\text{C}$	120	120	120
Drying time/s	35	45	35
Atomisation temperature/ $^{\circ}\text{C}$	2 600	2 660	2 800
Purge gas	Ar or N_2	Ar or N_2	Ar or N_2
Purge gas flow-rate/ ml min^{-1}	1 500	8	40
Purge gas pressure/ lb in^{-2}	20	20	20

Results and Discussion

In carbon furnace atomisation, atomic or molecular species formed from the injected sample are present in the tube atmosphere for only a short time. After release from the surface of the tube, such species are removed either by the flow of inert gas or by diffusion. It is therefore

difficult to obtain the spectrum of a molecular species over a wide wavelength range during a single atomisation. The spectra described in this paper were obtained by three methods. In the first, spectra were measured and plotted manually, each point being obtained during a separate atomisation. Although the spectra were obtained on instruments of moderate to high resolution, they are distorted by the lack of detail. They do, however, allow an accurate assessment of wavelengths of maximum intensity and an appreciation of the general structure of the molecular bands to be made. Several emission spectra were also measured on a spectrometer with a vidicon detector which allowed observation of 70-nm wavelength intervals to be made during a single atomisation. Finally, high-resolution spectra over a small wavelength range (1.0 nm) were obtained by using the wavelength modulation system and oscilloscope readout. The three sets of spectra provide useful correlation and provide data for general application in future studies of atomic emission from carbon furnace atomisers. In the measurement of species formed from the tube and its atmosphere, *e.g.*, the CN radical, no such difficulty exists, as this species is formed continuously while the tube is operated at high temperature. Such spectra were measured by the vidicon system and also by using the Monospek 1000 in the scanning mode. The spectra observed are discussed below.

CN Radical

Fig. 1 shows the spectrum recorded using the HGA-74 furnace and the Monospek 1000 for the wavelength range 375–390 nm. Three definite maxima are observed, which correspond to the 388.3-, 387.1- and 386.2-nm bands of the $B^2\Sigma^+ - X^2\Sigma^+$, $\Delta\nu = 0$ transitions.¹⁰ The (3,3) band head at 385.5 nm appears to be present as a shoulder only. A similar spectrum was reported by Massmann and Gücer.⁶ Fig. 1 shows the CN spectrum measured in nitrogen as before⁶ but also illustrates that a similar but much weaker (approximately 50 times weaker) emission signal is obtained when argon is used as the purge gas. Similar spectra were observed using an HGA-2100 with vidicon detector (Figs. 2 and 3). The vidicon spectrum in Fig. 2, using nitrogen purge gas, also clearly shows the $\Delta\nu = -1$ sequence of bands from 415.2 to 421.6 nm. In all instances, spectra of CN were measured at full or normal purge gas flow. Some nitrogen must therefore be present in the argon either as impurity in the argon, from air leaks in the furnace assembly or windows, or from degassing of the furnace following exposure to air.

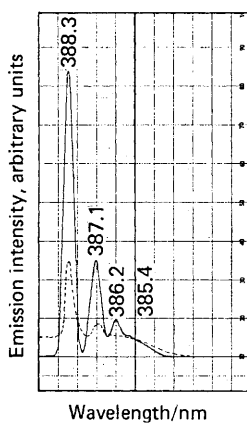


Fig. 1. Molecular-emission spectrum of CN radical in an HGA-74 graphite furnace, in nitrogen, at 2 660 °C, measured on a Monospek 1000 in the scanning mode, between 382 and 392 nm. A spectrum obtained in argon with intensity $\times 10$ is superimposed and shown as a broken line.

Additional peaks were observed for the $B\ ^2\Sigma^+ - X\ ^2\Sigma^+$ band from the $\Delta v = +1$ system at 359.0, 358.6 and 358.4 nm. These bands are shown clearly in Fig. 4, but are shown only as a single peak in the vidicon spectrum in Fig. 5. This is the first report of CN emission at this wavelength from the carbon furnace and the high gain required is illustrated by the general background levels observed in Figs. 4 and 5. A band also appears at 356 nm in Fig. 4, which is analogous to a band assigned to CN by Mavrodineanu and Boiteux,¹⁰ but not assigned to a specific transition. These bands were observed only when nitrogen was used as the purge gas.

C₂ Radical

The major band system of the C₂ radical observed in the carbon furnace is the Swan system, $A\ ^3\Pi_g - X\ ^3\Pi_u$. The vidicon spectrum in Fig. 6 shows the strong 516.5-nm band (0,0) and the weaker 512.9-nm band (1,1). Of greater significance analytically, however, is the fine structure which extends over the entire band system.

When wavelength modulation is used in furnace emission as a background correction system, the presence of sharp bands within the modulation interval can result in a degradation of detection limits, as the background will generate a signal, which will introduce a background-carried fluctuation noise component into the total system noise.¹⁵ In furnace emission, the background-carried noise will be an offset from zero intensity which may not be reproducible from run to run and whose intensity may mask the analyte emission intensity. The effect, however, which is essentially that of a spectral interference, can often be eliminated by proper adjustment of the modulation interval and slit width, as has been described previously.¹⁴ An example of such an interference is shown in Fig. 7 (an oscilloscope trace generated by the wavelength modulation system) where the 510.554 nm copper line is interfered with by C₂ band fine structure on either side.

Calcium Oxide Spectrum

Molecular emission bands were observed from calcium solutions in the 370–450-, 545–560- and 590–650-nm regions. Spectra from the latter two spectral regions were recorded point by point using the HGA-74 - Monospek system and were obtained by injection of 50 μ l of 2 000 μ g ml⁻¹ of calcium as calcium nitrate. The sample was dried and then atomised at 2 660 °C. The maximum emission intensity was plotted after subtraction of the tube background. The results are illustrated in Figs. 8 and 9 and show diffuse bands in both areas. Maxima in the 590–650-nm region are observed at the following wavelengths: 593.0, 610.4, 612.3, 616.1, 616.4, 617–618, 621.0, 630.6 and 634.0 nm.

These spectra correlate well with arc spectra described by Gaydon⁸ and Pearce and Gaydon¹¹ with the exception of the bands at 593.0 and 610–612 nm, which do not appear to have been reported previously. A vidicon spectrum from the HGA-2100 is shown in Fig. 10 for the 590–640-nm region using 100 μ g ml⁻¹ of calcium. The sodium doublet at 590 nm is also apparent in Fig. 10, and is caused by sodium contamination in the graphite tube. The spectra from the two instrument systems are similar. The similarity between the emission and absorption spectra is shown in Fig. 11. These spectra were measured using the HGA-72 furnace mounted in the PE306 spectrometer. The absorption measurements were made with a tungsten-filament light source. The 554-nm band interferes with the atomic-emission determination of barium in the carbon furnace but background correction for this band is possible by using wavelength modulation.⁹

The molecular bands observed from 370 to 450 nm are shown in Fig. 12. The calcium atomic line at 422.6 nm also appears in the scan. These bands correspond reasonably well to the blue system of CaO ($B\ ^1\Pi - X\ ^1\Sigma$) described by Pearce and Gaydon.¹¹ As a great number of useful emission analytical lines lie in this spectral region (*e.g.*, aluminium 396.2, manganese 403.1, chromium 425.4 and molybdenum 390.3 nm) care must be exercised when using background correction in matrices with high calcium content.

The self-reversal of atomic lines in the carbon furnace has been reported previously.^{3,6} This effect has been attributed to the optically thick atomic vapour cloud and the thermal gradient between the centre of the carbon tube and the ends. Self-reversal of the calcium oxide bands can also be observed, as shown in Fig. 13, at a concentration of 10 000 μ g ml⁻¹. A band at 581 nm, which was not apparent at lower concentrations, also appears.

Carbon furnace spectra from calcium molecules are different from flame emission spectra

that have been shown to be caused by CaOH molecules.¹⁶ Arc spectra have been ascribed to CaO or even Ca₂O₂¹¹ and either can cause the spectra observed in the carbon furnace. Flame and furnace emissions occur in the same wavelength regions and there appears to be considerable difficulty in assigning bands in systems other than flames in which the lower water concentration should reduce or inhibit the formation of CaOH. In the furnace very little water vapour will be present during the atomisation stage but it can appear in small amounts for the same reasons as mentioned for nitrogen in argon. Attempts to remove any last trace amounts of water in the argon purge gas by using magnesium perchlorate showed no changes in the spectra observed. It remains a possibility, however, that the observed spectra could be from two or more species such as CaO and CaOH in admixture and the presence of residual water vapour might explain the differences between Figs. 9 and 10.

Strontium Oxide Spectrum

When strontium solutions are atomised in a similar manner to calcium, a strong band is observed, with a maximum at 606.4 nm and shoulders at 601.9 and 605.4 nm, and a diffuse band is observed between 642 and 680 nm, with clear maxima at 650, 657 and 669 nm. These bands are illustrated in Figs. 14 and 15, which were obtained by using the Monospek 1000, and in Fig. 16 for the 640–680-nm region, which were obtained by using the vidicon system. A 50- μ l aliquot of 1 000 μ g ml⁻¹ of strontium as the nitrate was used in both instances.

The SrOH species is said to give a number of peaks in the 604–611-nm region in flames^{10,16} but the spectrum recorded, although it lacks definition, shows only one strong maximum and appears to be similar to the arc spectrum ascribed to SrO or to a more complex oxide reported by Charton and Gaydon.¹⁷ The maxima in the 650–685-nm region also appear, as expected, to be more similar to the arc spectrum than the flame spectrum of strontium. The 682-nm band, which is a very strong emission band in flames, appears to be relatively weak in furnace emission.

Magnesium Oxide Spectrum

Very weak emission was also observed from magnesium solutions by using the vidicon system. The spectrum illustrated in Fig. 17 was obtained only on injection of 50 μ l of 10 000 μ g ml⁻¹ of magnesium as magnesium nitrate into the HGA-2100 furnace. Several maxima can be identified, but the spectrum is partially distorted by self-absorption. The emission signal occurs in a similar region to that reported for an arc burning in oxygen or air.^{11,18}

The above spectra demonstrate the occurrence of molecular emissions from species formed in the carbon furnace from volatilisation of the furnace itself and from samples injected into it. Earlier work by King has shown emission from such oxide species from furnaces operated in an air atmosphere but it is shown that similar spectra are observed in the inert gas atmospheres used in modern analytical carbon furnace atomisers. In using carbon furnace systems for atomic-emission analysis, background emission from such species formed from the sample matrix must obviously be considered. In many instances a form of background correction such as wavelength modulation may remove this interference⁹ but if the emission band contains complex fine structure this correction can involve difficulties.¹⁴ Emission from molecular species will not be a significant problem in atomic absorption as most emissions are relatively weak and hollow-cathode modulation compensates for emission. In some instances, such as for the intense calcium oxide bands, the system noise may be increased and detection limits degraded by an increase in photomultiplier shot-noise.

The measurement of these spectra shows that oxide species are formed in the carbon furnace during atomisation of solutions of calcium, strontium and magnesium and this reaction may also be true for other elements. While it is possible that the molecules may be formed by reaction of atoms with trace amounts of oxygen present in the furnace atmosphere, it seems more probable that volatilisation of molecules directly from the sample matrix on the carbon tube is the mode of formation. Molecules formed in this manner may be dissociated in the vapour phase before being swept out of the furnace tube.

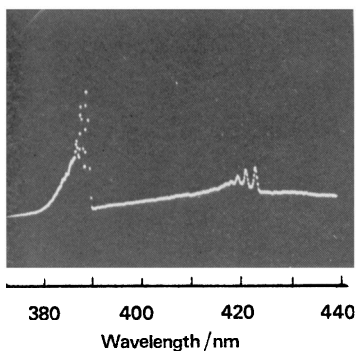


Fig. 2. Molecular-emission spectrum of CN radical in an HGA-2100 furnace at 2800 °C in nitrogen. Spectrum photographically recorded from a vidicon detector from 2 to 5 s after the beginning of the atomisation step.

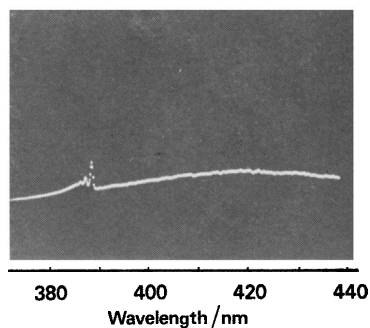


Fig. 3. Molecular-emission spectrum of CN radical in an HGA-2100 furnace at 2800 °C in argon. Spectrum photographically recorded from a vidicon detector from 2 to 5 s after the beginning of the atomisation step.

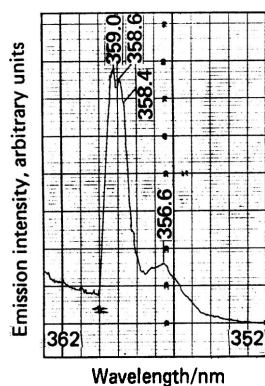


Fig. 4. Molecular-emission spectrum of CN radical in an HGA-74 furnace at 2660 °C in nitrogen, measured on a Monospek 1000 in scanning mode between 352 and 362 nm.

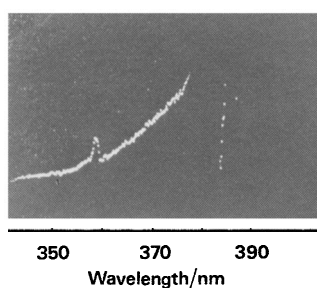


Fig. 5. Molecular-emission spectrum of CN radical in an HGA-2100 furnace at 2800 °C in nitrogen. Spectrum photographically recorded from a vidicon detector from 2 to 5 s after the beginning of the atomisation step.

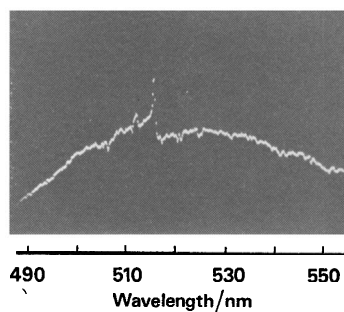


Fig. 6. Molecular-emission spectrum of C_2 radical in an HGA-2100 furnace at 2800 °C in argon. Spectrum photographically recorded from a vidicon detector from 2 to 5 s after the beginning of the atomisation step.

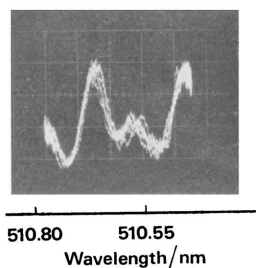


Fig. 7. Wavelength modulation spectral scan illustrating the interference of C_2 molecular-emission fine structure on the 510.554-nm copper transition. The photograph represents 20 μ l of copper solution, 1 000 μ g ml^{-1} , at approximately 3 s after the beginning of the atomisation step (2 800 $^{\circ}C$).

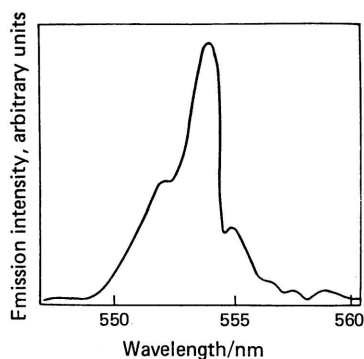


Fig. 8. Molecular-emission spectrum from 50 μ l of calcium solution, 2 000 μ g ml^{-1} , in the HGA-74 graphite furnace at 2 660 $^{\circ}C$ measured on a Monospek 1000 at 0.5-nm wavelength intervals.

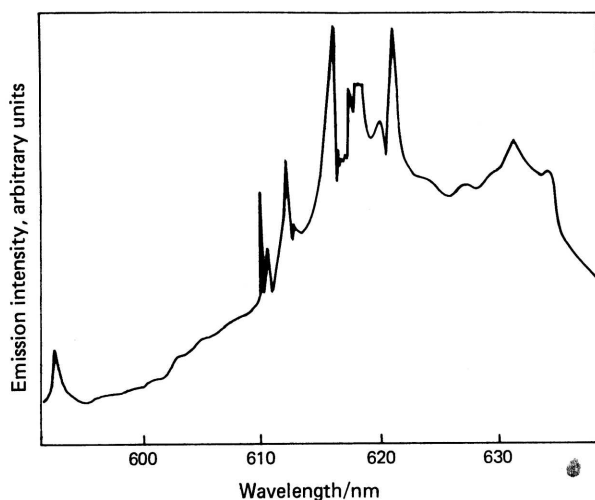


Fig. 9. Molecular-emission spectrum of 50 μ l of calcium solution, 2 000 μ g ml^{-1} , in the HGA-74 graphite furnace at 2 660 $^{\circ}C$, measured on a Monospek 1000 at 0.1-nm intervals around peak maxima and 0.5-nm intervals elsewhere.

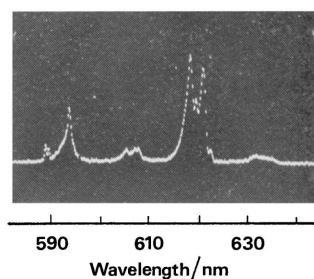


Fig. 10. Molecular-emission spectrum of 50 μ l of calcium solution, 100 μ g ml^{-1} , in the HGA-2100 graphite furnace at 2 800 $^{\circ}C$. Spectrum photographically recorded from a vidicon detector from 2 to 5 s after the beginning of the atomisation step.

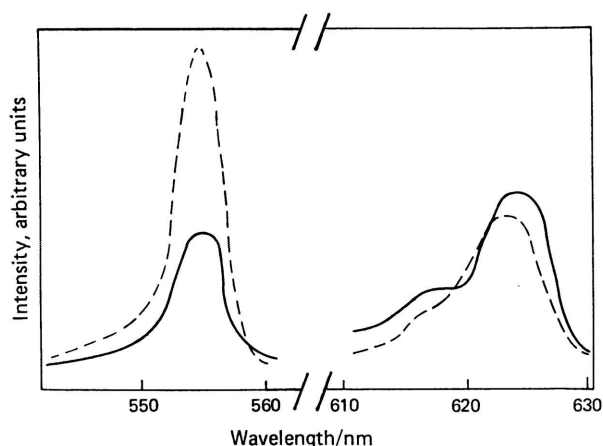


Fig. 11. Comparative molecular-absorption and -emission spectra of 50 μl of calcium solution, 4 000 $\mu\text{g ml}^{-1}$, on the HGA-72 graphite furnace at 2 600 $^{\circ}\text{C}$. Measured on a Perkin-Elmer 306 atomic-absorption/emission spectrometer at 1 nm wavelength intervals. Solid lines, absorption spectra; and broken lines, emission spectra.

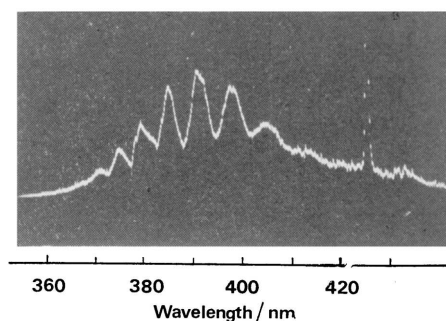


Fig. 12. Molecular-emission spectrum of 50 μl of calcium solution, 10 000 $\mu\text{g ml}^{-1}$, in the HGA-2100 graphite furnace at 2 800 $^{\circ}\text{C}$. Spectrum photographically recorded from a vidicon detector from 2 to 5 s after the beginning of the atomisation step.

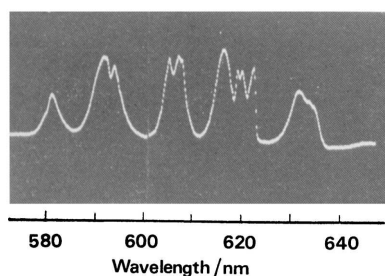


Fig. 13. Molecular-emission spectrum of 50 μl of calcium solution, 10 000 $\mu\text{g ml}^{-1}$, in the HGA-2100 graphite furnace at 2 800 $^{\circ}\text{C}$. Spectrum photographically recorded from a vidicon detector from 0 to 3 s after the beginning of the atomisation step.

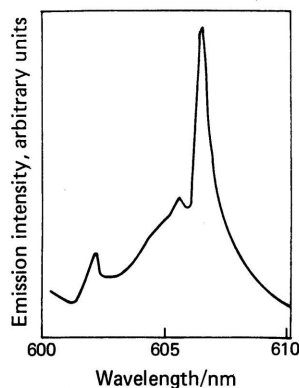


Fig. 14. Molecular-emission spectrum of 50 μl of strontium solution, 1 000 $\mu\text{g ml}^{-1}$, in an HGA7-4 graphite furnace at 2 660 $^{\circ}\text{C}$, measured on a Monospek 1000 at 0.1-nm wavelength intervals.

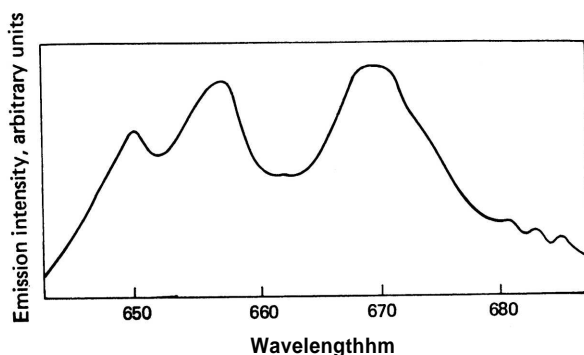


Fig. 15. Molecular-emission spectrum of 50 μl of strontium solution, 1 000 $\mu\text{g ml}^{-1}$, in an HGA-74 graphite furnace at 2 660 $^{\circ}\text{C}$, measured on a Monospek 1000 at 1.0-nm wavelength intervals.

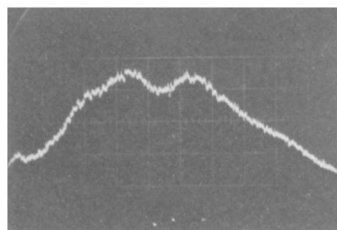


Fig. 16. Molecular-emission spectrum of 50 μl of strontium solution, 1 000 $\mu\text{g ml}^{-1}$, in an HGA-2100 graphite furnace at 2 800 $^{\circ}\text{C}$. Spectrum photographically recorded from a vidicon detector from 2 to 5 s after the beginning of the atomisation step.

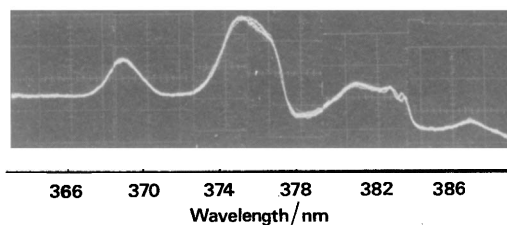


Fig. 17. Wavelength modulation spectral scan of molecular-emission spectrum from 50 μl of magnesium solution, 10 000 $\mu\text{g ml}^{-1}$, in the HGA-2100 graphite furnace. The spectrum is a composite of 6-nm scans using the 0.25-m monochromator with oscillating mirror and oscilloscope readout.

The authors thank G. Lehman and Princeton Applied Research for the short-term loan of the vidicon system. The mention of commercial equipment does not imply endorsement by the National Bureau of Standards.

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Received March 30th, 1977

Accepted April 26th, 1977