

Chemical Analysis by Observation of Spectra

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It is known that several substances have the property of producing certain bright lines when brought into the flame. A method of qualitative analysis can be based on these lines, whereby the field of chemical reactions is greatly widened and hitherto inaccessible problems are solved. We limit ourselves here to developing the method for alkali and earth-alkali metals and demonstrating its value by some examples.

The lines show up the more distinctly the higher the temperature and the lower the luminescence of the flame itself. The gas burner described by one of us (Bunsen, these Ann. 100, p. 85) has a flame of very high temperature and little luminescence and is, therefore, particularly suitable for experiments on the bright lines that are characteristic for these substances.

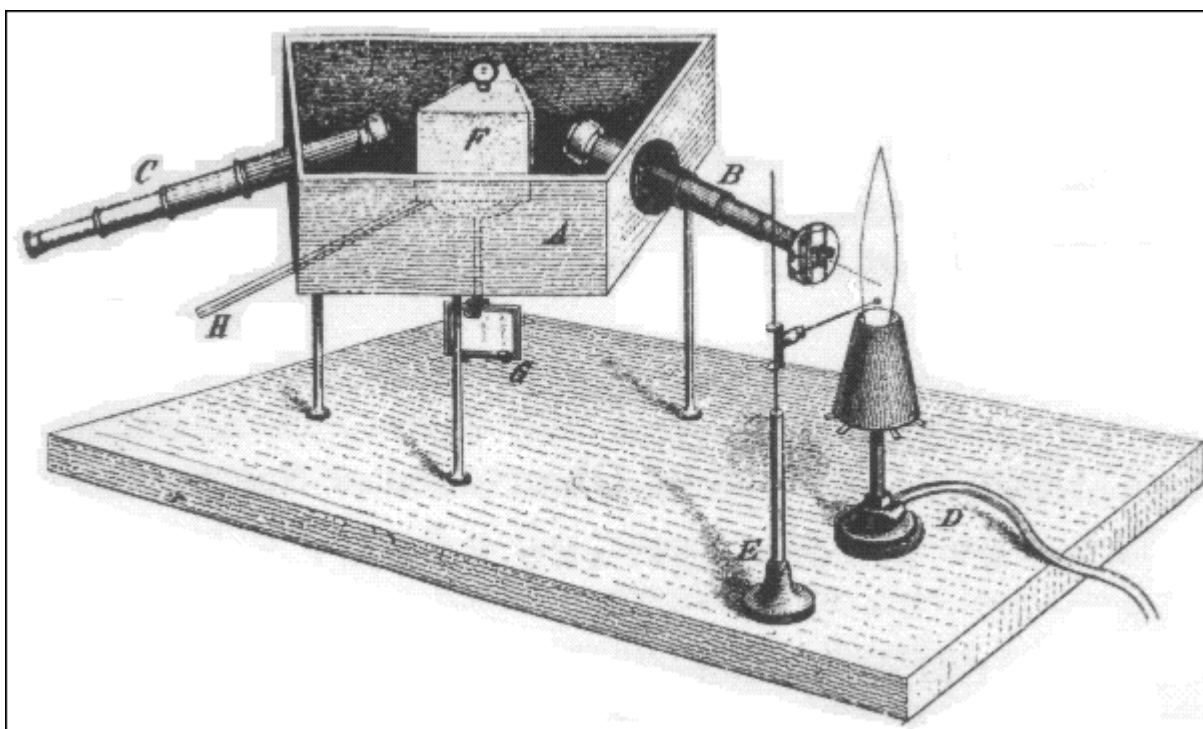


Figure 3-1 shows the apparatus we used for the observation of spectra. A is an internally blackened box with a trapezoidal bottom resting on three legs; the two oblique side walls, which form an angle of about 58° with each other, carry the two small telescopes B and C. The eyepiece of the first is removed and replaced by a plate in which a slit formed by two brass edges is adjusted at the focus of the objective lens. The lamp D is arranged before the slit so that the rim of the flame is on the axis of tube B. Somewhat below the spot where the axis meets the rim, there is the end of the loop formed in a fine platinum wire, which is held by arm E. The little pearl of the dry chlorine compound to be investigated is melted to this loop. Between the objective lenses of telescopes B and C is the hollow prism F of 60° refractive angle; it is filled with carbon disulphide. The prism rests on a brass plate that can be rotated on a vertical axis. This axis carries mirror G on its lower end and, above it, handle H by which prism and mirror can be rotated. A small telescope is directed toward the mirror so that the observer can see the horizontal scale mounted at a small distance. By rotating the prism, the entire spectrum of the flame can be brought before the hair line of telescope C Every place in the spectrum corresponds to a reading to be made on the scale. If the spectrum is very weak, the hairline in C is illuminated with the aid of a lens that throws part of the rays of a lamp through a small opening in the side of the ocular tube of C.

We have compared the spectra produced by the above-mentioned chlorine compounds with those obtained when the bromides, iodides, oxides, sulphates, and carbonates of the metals are brought into the flames of sulphur, carbon dioxide, aqueous alcohol, illuminating gas, carbon monoxide, hydrogen, and detonating gas.

In this time-consuming, extensive research, which need not be presented here in detail, it came out that the variety of the compounds in which the metals were used, the differences in the chemical processes of the flames, and the great difference between their temperatures had no influence on the position of the spectral lines corresponding to the individual metals.

Sodium

Of all spectral reactions, that of sodium is the most sensitive. Swan (these Ann. 100, p. 311) has already drawn attention to the smallness of the sodium chloride quantity that can still produce a distinct sodium line.

The following experiment shows that chemistry has no reaction comparable in sensitivity to this spectrum-analytical determination of sodium. In a corner of our 60 cu.m. room farthest away from the apparatus, we exploded 3 mg. of sodium chlorate with milk sugar while observing the nonluminous flame before the slit. After a few minutes, the flame gradually turned yellow and showed a strong sodium line that disappeared only after 10 minutes. From the weight of the sodium salt and the volume of air in the room, we easily calculate that one part by weight of air could not contain more than 1/20 millionth weight of sodium. The reaction can conveniently be noticed within a period of one second, and in this time only about 50 cc. or 0.0647 g. of air containing less than a twenty-millionth gram per gram pass through the flame, which means that the eye can perceive quite distinctly less than 1/3 millionth mg. of the sodium salt. With this sensitivity of the reaction it becomes understandable that only rarely is a noticeable sodium reaction absent in air at glowing temperature.

This sodium chloride content of the air, which can easily be proven by spectral analysis, deserves attention in another respect. If, as can now scarcely be doubted, there are catalytic influences that are responsible for the miasmatic spreading of diseases, then an antiseptic substance like sodium chloride could scarcely be without essential influences in the air, even if present only in minimal amounts. By daily and long-continued spectral observations, it will be easy to learn whether changes in the intensity of the spectral lines produced by atmospheric sodium compounds have any connection with the advent of endemic diseases or the direction in which they are spreading.

Lithium

The glowing vapor of lithium compounds produces two sharply defined lines: a yellow, weak $\text{Li}\beta$, and a red, strong $\text{Li}\alpha$. This reaction, too, surpasses all others known in analytical chemistry as to definiteness and sensitivity.

With this method, the unexpected fact can be stated beyond any doubt that in nature lithium is one of the most widely distributed substances.

It hardly needs to be remarked that the lines of lithium are shown by a mixture of sodium and lithium salts, side by side with the sodium reaction and nearly undiminished in sharpness and distinctness. When a pearl with a content of 1/1,000 lithium salt is brought into a flame, the red line of lithium appears, although the naked eye notices only the yellow light of the sodium without any reddish coloring. The sodium reaction persists somewhat longer, because the lithium salts are more volatile.

In the technical production of lithium compounds, spectral analysis offers a tool of inestimable value for selecting materials and processes.

Potassium

In the flame, the volatile potassium compounds give a very long continuous spectrum with only two characteristic lines: the first, $\text{K}\alpha$ is in the farthest red bordering on the infrared, exactly coinciding with the dark

line A of the sun spectrum; the other, $K\beta$ far in the violet and also coinciding with a Fraunhofer line. A very weak line, coinciding with the Fraunhofer line B, is visible from a highly intense flame, but not very characteristic.

Strontium

The spectra of all the alkaline earths are much less simple than those of the alkalis. Strontium is especially characterized by the absence of green lines; eight lines are very prominent, six red, one orange, and one blue.

Calcium

The calcium spectrum can be distinguished at a glance from the four discussed above because it has a very characteristic and intense line in green, $Ca\beta$. A second, no less characteristic, is the strong orange line $Ca\alpha$, much farther toward the red than the sodium line or the orange line of strontium.

Barium

The barium spectrum is the most complicated of the spectra of alkalis and earth alkalies. Different from the above-described are the easily recognized green lines $Ba\alpha$ and $Ba\beta$; they are more intense than all the others, the first to appear and the last to fade in a weak reaction. $Ba\gamma$ is less sensitive but still characteristic. The proportionately great extension of the spectrum makes the spectral reactions of barium compounds somewhat less sensitive than the others. In our room, 0.3 g. barium chlorate were burnt with milk sugar; after the air had been thoroughly mixed by means of an open umbrella, the $Ba\alpha$ line was distinctly visible for some time. From a calculation like that carried out for sodium, it can be concluded that less than 1/1,000 mg. is indicated by the reaction.

Spectrum analysis should become important for the discovery of hitherto unknown elements. If there should be substances that are so sparingly distributed in nature that our present means of analysis fail for their recognition and separation, then we might hope to recognize and to determine many such substances in quantities not reached by our usual means, by the simple observation of their flame spectra. We have had occasion already to convince ourselves that there are such now unknown elements. Supported by unambiguous results of the spectral-analytical method, we believe we can state right now that there is a fourth metal in the alkali group besides potassium, sodium, and lithium, and it has a simple characteristic spectrum like lithium; a metal that shows only two lines in our apparatus: a faint blue one, almost coinciding with Sr, and another blue one a little further to the violet end of the spectrum and as strong and as clearly defined as the lithium line.

Spectrum analysis, which, as we hope we have shown, offers a wonderfully simple means for discovering the smallest traces of certain elements in terrestrial substances, also opens to chemical research a hitherto completely closed region extending far beyond the limits of the earth and even of the solar system. Since in this analytical method it is sufficient to see the glowing gas to be analyzed, it can easily be applied to the atmosphere of the sun and the bright stars. However, a modification is here necessary, because of the light emitted by these stars. One of us in his work "on the relationship between emission and absorption of bodies for heat and light" (Kirchhoff, these Ann. 109, p. 275) has proved theoretically that the spectrum of a glowing gas is reversed; i.e., the bright lines are converted into dark ones, in case it has behind it a light source of sufficient intensity and sending out a continuous spectrum. It can be concluded that the spectrum of the sun with its dark lines is just a reversal of the spectrum which the atmosphere of the sun would show by itself. Therefore, the chemical analysis of the sun's atmosphere requires only the search for those substances that produce the bright lines that coincide with the dark lines of the solar spectrum.

For example, the bright red line in the spectrum of a gas flame into which some lithium chloride has been brought changes into a black line when full sunlight is transmitted through the flame.