

Note on a Method of Observing the Flame Spectra of Halogen Salts

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XXIV. *Note on a Method of Observing the Flame Spectra of Halogen Salts.* By E. N. DA C. ANDRADE, B.Sc., Ph.D., 1851 Exhibition Scholar of the University of London.

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§ 1. It has been shown by Smithells* that if chlorine be introduced into a flame containing the luminous vapours of certain metals—*e.g.*, lithium or strontium—it destroys the coloration. To demonstrate this it is best to introduce the salt by means of a Gouy sprayer; the effect can then be shown by passing the air supplied to the burner over chloroform. The effect cannot be shown by introducing a bead of the salt into the chlorinated flame, because the great volatility of the chloride formed causes the metal to vaporise so much faster that the chlorine is no longer present in sufficient excess to ensure the greater part of the vaporised metal being chemically combined. If the salt be sprayed, however, the amount of metallic vapour present is not affected by the introduction of the chlorine, which then completely extinguishes the colour.

§ 2. When introducing a bead of salt into a chlorinated flame on a nickel wire, I noticed that the nickel wire coloured the flame independently of the presence of any salt. This led me to introduce wires of other metals into the chlorinated flame, in the hope, afterwards justified, of obtaining characteristic spectra. The effect is very striking with copper. An ordinary copper wire in the chlorinated flame gives an intense blue in the lower part of the flame and a strong red in the upper part; the spectrum turns out to be the same as that obtained in another way for copper chloride by Smithells,† and investigated in detail by him. The method described allows the different emissions in the different zones of the flame to be shown remarkably clearly.

§ 3. I divide the flame into four parts: the edge E, the outer mantle M_1 , the inner mantle M_2 , and the cone C (Fig. 1). Copper gives in the edge a red coloration, in the outer mantle blue; the inner mantle is in general uncoloured. If the wire be held in the cone, however, a streak of blue vapour rises from it

* Smithells, Dawson and Wilson, "Phil. Trans.," 193A, 1900, p. 121. There is here a reference to a previous Paper by Smithells which contains a brief remark on the point in question.

† Phil. Mag." (V.), 39, p. 122, 1895.

into the inner mantel. Holding the wire through the flame just touching the cone, all these colorations can be seen at once in their respective zones, the division being very clearly marked.

The other chloride spectra which I have so far observed are those of nickel, cobalt and iron, the flame spectra of which do not seem to have been fully observed before in the cases where they have been observed at all. Introducing a nickel wire into the chlorinated flame I find in the edge a green coloration, in the outer mantle lavender, from the cone pink.*

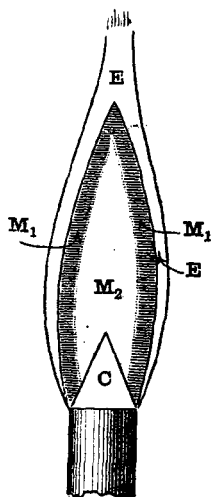


FIG. 1.

Not having cobalt wire, I introduced the glowing salt, which gives no colour in the ordinary flame, on a platinum wire. The flame is then red in the edge and a bluish pink in the outer mantle. Iron gives a yellow coloration, not due to traces of sodium.

§ 4. By heating the wires electrically while they are in the flame it can be shown that the emissions are probably not temperature effects. For instance, the wires may be heated electrically to melting in the edge of the flame without changing the character of the emission; its intensity increases somewhat with rise of temperature, however.

* P. J. Hartog (British Assn. "Report," 1901, p. 613) makes mention of a red coloration from the cone, and a *temporary* purple which flashes out and disappears.

§ 5. The chloride spectra obtained in the manner described have certain general characteristics. In all cases there is a continuous background; further, the spectra are banded spectra. Copper chloride, as is well known, shows brilliant bands in the blue and green with a faint continuous background; the green bands are due to the oxide, according to Smithells (*loc. cit.*). The red coloration in the edge gives a continuous spectrum. With nickel the green in the edge is continuous; we have for the spectra in other parts of the flame a continuous background, with bands in the red, blue-green and violet. The red bands are strong in the cone and cause the pink tint. With cobalt there is a red continuous spectrum in the vapour in the edge of the flame, a continuous spectrum with bands in the green and blue superposed on it for other parts of the flame. With iron, apparently in any part of the flame, we have a continuous background with bands in the red, green and yellow, the strongest being the yellow band. It seems that for the different metals the continuous background has its maximum intensity in different places characteristic of the particular metal, as Lenard* has shown to be the case for the continuous backgrounds of the alkali metals. The fact that all these spectra are banded accords with the view that banded spectra may be attributable to molecules, line spectra to atoms.

Attempts have been made to get chloride spectra of tin, lead and mercury by bringing the vapours of these metals into the flame. Characteristic colorations are produced, but at present have not been resolved spectroscopically.

§ 6. I have made some experiments with flames into which the vapours of bromine and iodine respectively have been introduced. A very small amount of bromine vapour is sufficient to extinguish completely the strong colour produced by sprayed solutions of lithium salts. Iodine vapour produces the same effect. Wires of some of the metals already mentioned give characteristic spectra in these flames; these await further examination.

§ 7. A few observations have been made on the deviation in an electric field of the luminous streak of chloride vapour. Lenard† showed in 1902 that the luminous vapour from a bead of salt in a flame is deviated in an electric field, the amount of deviation depending on the metal (and, of course, on the

* "Annalen der Physik" (IV.), 17, p. 208, 1905.

† "Annalen der Physik" (IV.), 9, p. 642.

upward velocity of the flame gases, and the strength of the field). G. Ebert in 1911 showed that in the case of strontium this deviation decreased when the vapour was decolorised by chlorine in the flame, tending to become zero as the intensity of coloration decreased. Lenard remarked that copper chloride is deviated in the electric field; he apparently used a bead of the salt, and does not mention the different colorations. From present observation it seems that the red colour is deviated partly to the positive and partly to the negative electrode. The blue goes mainly to the negative electrode. The deviation is, however, especially marked in the blue vapour from the cone, the vapour behaving as if strongly positively charged. Similar results are found for nickel. There is no doubt that the luminous chloride vapour is strongly charged, the carriers (which emit band spectra) being mainly positive, but negative also existing.* Very rough estimates of the velocity of migration of the carriers show that the carriers probably alternate the positive state with the neutral, as assumed by Lenard for the carriers of the line spectra.† As we do not yet know in which state the carriers actually emit the light, we cannot, however, confirm or contradict Stark's assumption that the carriers of the band spectra are neutral.‡

§ 8. This preliminary note calls attention to the two classes of metallic chlorides:—

1. Those which are non-luminous in the flame; this class apparently consisting of the alkaline and alkaline earth metals.
2. Those which give characteristic banded spectra with continuous grounds.

A new modification of method has been described for obtaining halogen compound spectra of some metals, which enables us to examine with ease the emission of the different flame zones, and has led in some cases to spectra apparently new. The electrical behaviour can also be easily examined by this method. It has been pointed out that, while the vapours of non-luminous chlorides are unchanged, the luminous chloride vapours are strongly charged. I hope to study in more detail the structure of the spectra of the different halogen salts, and the electrical behaviour of the vapours, with a view to getting information on the mechanism of the emission of banded spectra.

* Cf. E. N. da C. Andrade, "Phil. Mag.," July, 1912, p. 16.

† *Loc. cit.*, 1902.

‡ See "Atomdynamik," Vol. II., p. 138.

ABSTRACT.

If a flame containing a large amount of chlorine be prepared by passing the air supplied to a colourless gas flame over chloroform, wires of certain metals—copper, nickel, iron, for instance—held in the flame give characteristic colorations in the different zones of the flame. These are due to the chlorides of the metal, which can exist undissociated, in some zones of the flame at least, in the presence of excess chlorine. The chloride spectrum of copper is well known (of Smithells) but the chloride spectra of nickel, cobalt, and iron chloride do not seem to have been fully observed before. The method makes it easy to observe the different emissions which take place in the different zones, and also the electrical migration of the vapour discovered by Lenard in 1902. All the chloride spectra have certain common characteristics. Attention is called to the fact, discovered by Smithells, that for the vapours of some metals—*e.g.*, lithium, strontium—the coloration produced in the flame is destroyed by chlorine. In such cases the vapours are not electrically charged, while in the case of the metallic chlorides which give characteristic spectra in the flame the vapours are strongly charged.

By bringing wires into flames containing bromine and iodine compound spectra were observed in some cases.

DISCUSSION.

Mr. A. CAMPBELL asked if Dr. Andrade could give an explanation of the blue coloured flame obtained when NaCl is thrown on to a fire.

The AUTHOR replied that the flame was the spectrum of copper chloride, there being a sufficient impurity of copper in the coal.