SECTION I

FLAME SPECTROSCOPY

The influence of the flame characteristics on the emission

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1. Premises

IN a flame photometer a flame is used for (1) transforming the sample to be analysed from the liquid or solid state into the gaseous state, (2) for decomposing the molecular compounds of the investigated element into simpler molecules or atoms, and finally, (3) for exciting the latter particles to light-emission. We shall be mainly concerned with the latter two functions of the flame, in discussing the influence of the flame characteristics on the emission.

It may be noted that the function of light-excitation is not as evident as it may seem to be at first sight. Recently the possibility of *absorption*-flame photometry was pointed out [1, 2], in which the absorption power and not the emission power of a flame is a criterion for the content of the sprayed sample. Because of its advantages the absorption method for flames is expected to become important in the future. In the following it will be disregarded, however.

When speaking of a flame, we have in mind the *"body,"* that is the burnt gas-mixture, well above the first reaction zone of a continuously burning gas flame. In this part of the flame a certain homogeneity of properties, as well as fair thermal equilibrium may be assumed to exist. An exception should be made, of course, for the radiation density, which must deviate from thermal equilibrium, as otherwise the flame would be essentially unsuitable for quantitative or even qualitative spectrochemical analysis.

The spectral radiation density in the flame deviates from the equilibrium value at flame temperature, in so far as the radiation emitted by a subvolume of the flame exceeds the radiation absorbed by this volume. In the interior parts of the flame and at wavelengths at which the absorption coefficient is large, this deviation will be small. It has been proved [3] for a flame actually used in flame photometry, that under usual conditions this deviation has a negligible influence on the emission power of the flame (and on the measured reversal temperature).

As an *Introduction* the subject of this paper, indicated above, may seem of somewhat restricted scope. Indeed, the more technical aspects of flame photometry, such as sprayer, filtering, etc, will be left out of account here. However, most of the more fundamental concepts and problems concerning the flame, will pass in review here when giving an answer on the present central question, which may be formulated as follows: "why, in which respect and to what extent does the emission behave differently in different flames?"

In answering this question, we shall consider preferably those properties of the flame emission that are nowadays more or less clearly understood on the basis of ionization, molecular dissociation and self-absorption.

We shall proceed by first establishing the characteristics that describe a flame (Sect. 2). Next we shall expose the different items that may be covered by the term "flame emission" (Sect. 3). Before passing to the proper discussion of the subject (Sect. 5), some essential facts about ionization, molecular dissociation and self-absorption will be briefly reviewed (Sect. 4). As a conclusion some remarks of a more general kind will be made (Sect. 6).

2. Specification of flame characteristics

Flames show a variety of individual forms: they may be rich or lean, thick or thin. In trying to characterize flames in their individuality some normalization will be first introduced, in so far as each flame is supposed to be fed by an air or oxygen flow of *unit* strength. So, all differences in oxygen consumption and in sprayer performance, which depends on the air or oxygen flow, are eliminated. Any actual flame which is fed by an air-flow of different strength, say 3 for instance, may always —in mind and in first approximation—be decomposed into three normalized flames in parallel which have the same characteristic properties as the original flame, except for the less essential cross-section.

A (normalized) flame may now be described by the following characteristic properties:

(1)   the *composition of the burnt gas-mixture*, including the content of free flame electrons produced by ionization of the burnt gases, occurring also when no metal is supplied to the flame;

(2)   the *temperature* of the flame, which—in first approximation—is supposed to be uniform over the flame cross-section and over most degrees of freedom;

(3)   the dimensions of the flame *cross-section*;

(4)   the *dilution factor* of the air containing the spray, that is the ratio of the volumetric flow of the air leaving the sprayer, to that of the burnt gas mixture in the flame.

The significance of the first three characteristics is obvious. It may be noted, that in first approximation the dilution factor is the only quantity that determines the content of element in the flame for a given content of element in the air-stream leaving the sprayer. Spray losses in the burner due to salt deposition, or in the flame due to radial diffusion of the metal vapour, will be disregarded here.

The above set of characteristics is sufficiently complete to define the conditions of a flame, as far as these conditions are important with respect to emission effects relevant in flame photometry. It may be remarked that the velocity of the flame gases is implicitly determined by the data just given, so it need not be added as another characteristic.

Of course, some of the characteristics listed may vary with height above the first combustion zone. However, this feature may be disregarded in most cases, when only a general view is desired.

3. Specification of emission characteristics

The aspects of the flame emission appearing to be relevant in flame photometry, are:

(1) the *absolute emission power* of the investigated element, that is the light flux in absolute units emitted at a chosen wavelength by the atoms or molecular compounds of the element. We may propose as an adequate measure for the emission power: the surface brightness, that is defined as the light flux emitted per unit solid angle through one square cm flame surface, in a direction perpendicular to this surface;

(2) the *line-to-background ratio* for a line or band of the investigated element, in a specified range of the spectrum;

(3) the *interference* with the emission of the investigated element caused by the presence of other *cations*;

(4) the *interference* with the emission of the investigated element caused by *anions* present in the sprayed solution;

(5) and finally, the *form* of the *calibration curve*, that is the plot of element emission against concentration.

Clearly, further interesting aspects might be suggested. For example, mention could be made of the stability of the emission of the investigated spectral line, or of the background radiation. Stability which is, indeed, problematic in electric arcs, is usually satisfactory in flame photometry, so it is not so urgent here. Besides it is for a great deal related to the spraying process (cf. [4], p. 78) which is beyond the scope of this discussion.

For the latter reason, also interference effects caused by adding alcohols to the solution, will be disregarded here. For simplicity's sake, also second order interferences (i.e. interferences with an interference), will be left out of account. An example of this type of interference was reported by STUMPF [5] for the case that aluminium is added to a solution of potassium and sodium salts.

It is obvious that the emission characteristics listed are not only dependent on the flame properties, but are also essentially to be considered as a function of the concentration, or range of concentrations, in the sprayed solution.

4. Ionization, dissociation and self-absorption

Both ionization and molecular dissociation are controlled by the law of mass action, which holds when an equilibrium state has been reached. According to this law, the product of the concentrations of the dissociation products is proportional to the concentration of the undissociated substance. So in the case of sodium chloride, one has:

$$[Na] \times [Cl]/[NaCl] = C_{NaCl \rightleftharpoons Na + Cl}$$

Or, in the case of ionized potassium, one has:

$$[K^+] \times [e]/[K] = C_{K \rightleftharpoons K^+ + e}$$

In both cases the equilibrium constant depends only on the kind of process involved and on the temperature. The constants may be calculated from a formula derived from statistical mechanics, which involves, among others, the dissociation or ionization energy as a characteristic parameter (cf. for a general survey: [6]).

Obviously, ionization reduces the content of free metal atoms in the flame, and as a result, it decreases the emission power of the atomic spectral lines. In the case of an alkali element, where the ion hardly emits any radiation because of its

peculiar structure, ionization implies necessarily a loss in flame-photometric sensitivity.

It follows immediately from the law of mass action, that an increase in content of free electrons represses the degree of ionization, and enhances the atomic emission power. So adding sodium to a potassium solution may increase the intensity of the atomic potassium lines. For sodium will produce free electrons in the flame, which have the mentioned effect on potassium that is partly ionized. A demonstration of the enhancement of the potassium emission by sodium is given in Fig. 1, in which the potassium calibration curve is plotted with different amounts of sodium added.
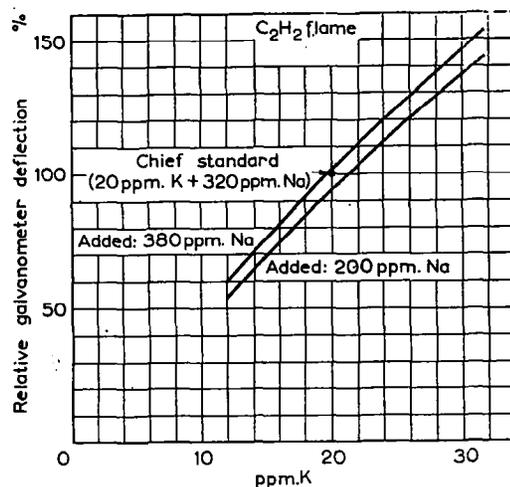

Fig. 1. Calibration curves for potassium in an air-acetylene flame with different amounts of sodium added, showing the positive sodium interference due to a shift in ionization equilibrium. Deflections are expressed as percentage of a "chief standard" deflection.

Many other examples of positive cation interference reported in the literature can be reasonably well explained by such a shift in ionization equilibrium (cf. [4], p. 147).

Also formation of molecular compounds in the flame may weaken the emission power of the atomic spectral lines. Since, however, the molecules formed may also emit spectral light, a loss in flame photometric sensitivity need not necessarily be associated with molecule formation. When an anion, such as chlorine, is added to a solution of some metal salt, the formation of metal chloride in the flame may cause a typical anion interference effect.

As another consequence of the law of mass action a curvature in the calibration curve may result since the content of emitting atoms may not be proportional to the total elemental content in the flame. This total elemental content in the flame is proportional to the solution content plotted as abscissa in the calibration graph. In the case of e.g., ionized potassium, it follows from the mass action law that:

$$1 - [\mathrm{K}]/[\overline{\mathrm{K}}] = (C/2[\overline{\mathrm{K}}])(\sqrt{1 + 4[\overline{\mathrm{K}}]/C} - 1)$$

if $[\overline{\mathrm{K}}]$ = total potassium content $\equiv [\mathrm{K}] + [\mathrm{K}^+]$, and C = ionization constant. It

is supposed that $[K^+] = [e]$, i.e. all free electrons present are produced by ionization of potassium.

The right-hand side of the above formula is easily shown to decrease monotonously from unity to zero when $[\overline{K}]$ increases from zero to infinity. So $[K]/[\overline{K}]$ increases monotonously with increasing $[\overline{K}]$, from which a concave curvature in the the calibration curve follows (if self-absorption is absent).

In Fig. 2 this typical concave curvature is clearly seen in the potassium calibration curve for the acetylene flame at which ionization has become noticeable because of the higher temperature.
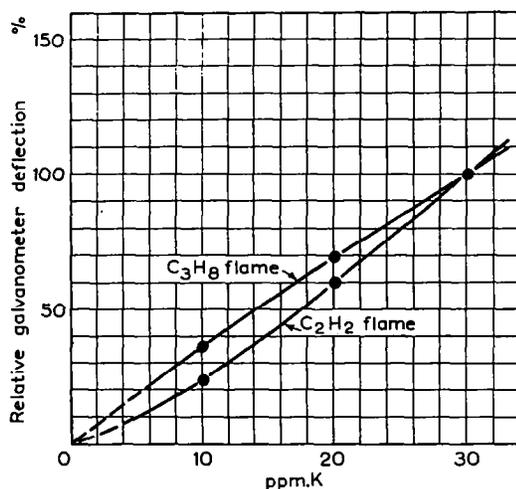

Fig. 2. Calibration curves for potassium (no other elements added), showing the occurrence of concave curvature, with the hotter flame, due to ionization.

Other examples of such curvature, which is rather more pronounced in the lower concentration range where ionization is higher, are often found in the flame photometric literature.

Self-absorption is another effect that may cause a curvature of the calibration graph. Self-absorption is based on the fundamental property of atoms emitting radiation at some wavelength, that they are also capable of absorbing radiation of the same wavelength. As a result, part of the yellow light emitted, for example, by excited sodium atoms, will be absorbed by other sodium atoms in the ground state. This results in a weakening of the net flame emission, because usually only a small fraction of the absorbed energy will be re-emitted again as radiation.

The fraction of radiation that is lost by self-absorption depends on the concentration of atoms in the ground state, which again depends on the content of the sprayed solution. This variation of the absorbed fraction with solution content causes the well-known convex curvature in the calibration curve.

At sufficiently high concentrations (i.e. with appreciable self-absorption), the flame emission increases as the square root of the solution content, according to classical theory (cf. also reference [7]). The deviation from this square-root-law for very high concentrations, predicted by a quantum mechanical refinement given by

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LINDHOLM [8] and HULDT [9], will not be further discussed here. A deviation from the square-root-law may also occur owing to a *self-reversal* effect in flames which are not shielded by a colourless border (cf. [32]).

Spectral lines other than resonance lines, that is to say, which have their lower state different from the ground state, show usually much less self-absorption, and consequently their calibration graph is not curved at higher concentrations.

5. The influence of the flame characteristics on the emission characteristics

The discussion will be given by considering separately the specific influence of each flame characteristic on one of the emission characteristics, The other flame characteristics are then in each case supposed to remain constant.

5.1. The influence of the *flame composition* on the emission. Typical components of the burnt gas mixture may be such particles as atomic or molecular hydrogen or oxygen, the neutral or negatively charged hydroxyl radical and free flame electrons.

5.1.1. These components may influence in several ways the *absolute emission power* of the flame. For example, the presence of oxygen or hydroxyl may induce the formation of oxides or hydroxides. In the case of alkali metals, this molecule formation may weaken the emission intensity of the atomic spectral lines, which are usually chosen as analysis lines. SMITH and SUGDEN [10, 11] have obtained evidence that hydroxide formation will be noticeably smaller with potassium and sodium than with the less common elements caesium, rubidium and lithium. We were able to find also some indirect evidence that sodium is not likely to be bound to molecules in a propane-air and acetylene-air flame (cf. reference [4], p. 76).

Alkaline-earth metals have more tendency to form molecules than the alkalis. Accordingly, they are often determined by means of their band spectrum. It is a remarkable fact that there is but limited certainty as to the type of molecule that emits the visible band spectrum which is usually chosen for analysis. Conclusions could be drawn in this respect only to a limited extent by JAMES and SUGDEN [12], and by LAGERQVIST and HULDT [13]. There is evidence that emission by chlorides of alkaline-earth metals in the flame is of little importance anyhow (cf. [14]).

Since the partial pressures of molecular compounds obtainable in the flame are certainly considerably below saturation pressure, loss in emission should not necessarily be expected if the melting or boiling temperature of these compounds happen to exceed the flame temperature. At least, if the equilibrium state is reached without a noticeable delay in time.

The free electrons which appear to be produced by the burnt gases of hydrocarbon flames (cf. reference [15]), will repress the ionization of the metal atoms in the flame, and will enhance the atomic emission power. This follows immediately from the mass action law, as we have seen before.

It may be noted that the content of flame electrons ($\sim 10^{11}$ cm^{-3}) produced by the flame gases exceeds considerably the equilibrium content, at least in nonluminous flames (cf. also [6]). We will not go into the problem of their origin here.

In a particular case we were able to correlate, indeed, the decrease in atomic emission power of potassium as a function of height above the combustion cones, with a decrease in content of flame electrons with height (cf. reference [4], p. 71]. This decrease in content of flame electrons

with height, indicates the occurrence of a slow recombination process, and stresses the hypothesis of their nonequilibrium state.

The formation of negative ions due to the capture of electrons by flame components, is expected to have an opposite effect as the presence of free flame electrons. The results concerning negative oxygen and hydroxyl ions found by GAYDON [15], and SMITH and SUGDEN [10] respectively, may not yet be accurate enough for a prediction of their actual part played in flame-photometry.

5.1.2. The influence of the flame *composition* on both *cation* and *anion-interference* is next to be discussed. When cation-interference occurs owing to a shift in ionization equilibrium, the presence of free flame electrons may buffer this interference, as they repress the ionization of the disturbing and of the disturbed element. In a particular case of sodium-potassium interference we could, indeed, check this buffering effect of the flame electrons (cf. reference [4], p. 141).

Buffering by flame-electrons may also explain why, e.g., SCOTT and co-workers [16] found the positive cation interference due to ionization to be smaller in the lower concentration range. For, at a lower salt-concentration, the flame electrons will be present in a comparatively larger excess, and their buffering influence will, accordingly, be greater.

A similar buffering effect was reported by FISCHER [17]. In this case no flame electrons, but electrons produced by ionization of caesium, which was purposely added to the sprayed solution, have also appeared to reduce the mutual interference between cations.

Components of the flame gases may influence also the extent of *anion interference*. It has appeared that the depressing effect of added hydrochloric acid on the intensity of atomic alkali lines is considerably less than would be expected on account of alkali-chloride formation alone. This discrepancy is easily explained by allowing for the presence of hydrogen in the flame, combining with part of the chlorine in the flame as hydrochloric acid. The removal of chlorine by the formation of hydrochloric acid will repress the formation of alkali chlorides, so that more alkali atoms are available for light-emission. This interference of hydrogen with the formation of alkali halides was already observed in 1939 by MANDELSTAM [18]. A direct and beautiful demonstration of the influence of hydrogen on the sodium emission has been given by ARTHUR and co-workers [19].

In an experiment we obtained the remarkable result that the extent of chlorine interference with alkali metals was still less than expected, even when the formation of hydrochloric acid molecules in the flame was allowed for (cf. reference [4], p. 164). This discrepancy may be related to an abnormally high content or energy of the hydrogen atoms, for which evidence was also found by BELCHER and SUGDEN [20] [34].

5.1.3. It has been shown above that a curvature in the *calibration curves* may in general, be caused by molecule formation or ionization, according to the law of mass action. However, it follows simply from the same law that an approximate proportionality between atomic content and total element content in the flame will exist, if the anion, or the free electrons respectively, are present in large excess, So a curvature in the calibration curve due to oxide or hydroxide formation will be hardly observed, since oxygen and hydroxyl always occur in comparatively large excess in the flame.

When in the flame free electrons are present in excess, they will swamp the curvature in the calibration curve which is connected with ionization.

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We have, actually, found a striking difference in curvature with potassium, when the curve was measured just above the combustion cones as well as at some distance above them (cf. reference [4], p. 140). This difference in curvature could be explained quantitatively by a variation in content of free flame electrons as a function of height.

5.2.1. Attention may be paid now to the most important parameter of a flame: the *temperature*. This parameter is of primordial importance, because it mainly determines the accessibility of elements and spectral lines to flame-photometric analysis.

In order to understand the part played by the temperature in flame emission, it may be useful to recall some basic facts. The intensity of an atomic spectral line in the flame depends on the following factors:

(1) the fraction of introduced salt that is evaporated (evaporation factor);

(2) the fraction of salt molecules that are dissociated (dissociation factor);

(3) the fraction of the atoms formed by dissociation that are *not* ionized (non-ionization factor);

(4) the fraction of the nonionized atoms that are excited (excitation factor);

(5) the probability of a transition from the excited state to the lower state;

(6) the energy of the light-quantum;

(7) finally, the self-absorption factor, that accounts for the fraction of emitted energy that is lost by self-absorption.

For the moment we will omit the evaporation factor, which may be important only in a special case, to be discussed later (cf. 5.2.2). The transition probability and the energy of the light-quantum are typically temperature-independent. The explicit dependence of the self-absorption factor on temperature will be of little importance in most cases. Of course, there is also an implicit dependence on temperature, because of the dependence of self-absorption on the atomic content, which may vary with temperature. It may be remarked that the change in emission power due to a change in atomic flame content, will always be partly compensated by the correlated change in self-absorption.

When dissociation is rather complete, and ionization not yet important, the variation of emission power with temperature is mainly controlled by the excitation or Boltzmann factor $e^{-E/kT}$, which depends exponentially on temperature T (with k = Boltzmann constant, and E = energy level of excited state). This exponential dependence accounts for the success of hot flames in exciting spectral lines corresponding to high energy levels (compare VALLEE's report [21] on the cyanogen flame).

The emission power of elements with low ionization potential (which are easily ionized) appears to increase much *less* with temperature than it would be expected from the Boltzmann factor just mentioned, It has even been reported [22], that the emission power of such elements is *reduced* by using a hotter flame, whereas the emission power of other elements increased considerably. This is easily explained by the increase in ionization at higher temperature. It should be kept in mind that the ionization constant contains a factor $e^{-W_i/kT}$ (W_i = ionization energy), increasing exponentially with temperature. Now, since the ionization energy is necessarily higher than the excitation potential of the atomic spectral line, it may occur, in

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principle, that ionization is the more important factor in the temperature dependence of the emission power.

The molecular *dissociation* constant involves also a factor which increases exponentially with temperature. Since dissociation favours the atomic emission power, an increase in temperature will here have an effect opposite to that of the ionization. This may explain why the gain in atomic emission power of Ca, for example, obtained by using a hotter flame may exceed the increase in excitation factor only.
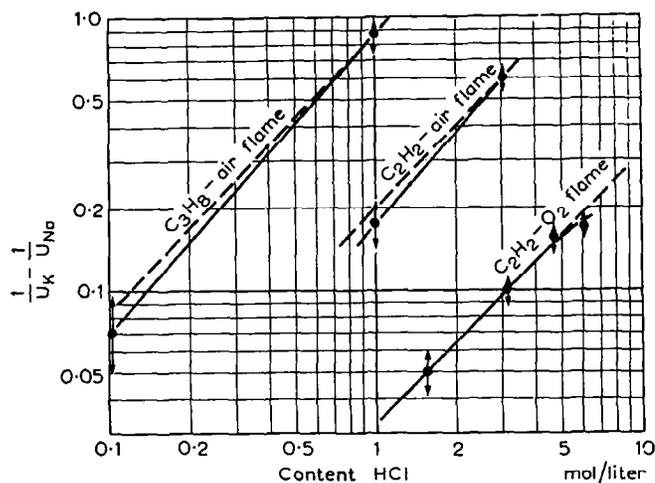

Fig. 3. $(1/u_K - 1/u_{Na})$, which is a measure for the formation of alkali chlorides in the flame (with u_K and u_{Na} being the potassium and sodium deflections in relative measure), is plotted against the content of hydrochloric acid added to the sprayed solution. The curves for the propane-air, acetylene-air and acetylene-oxygen flame (with increasing temperatures!) were derived from the experimental results obtained by BREALY *et al.* [29], SCHUFFELEN [30] and SCOTT *et al.* [16] respectively. Note that the slope of the curves approaches fairly the theoretical value of 45° (indicated by broken lines).

5.2.2. From what has been said about the dependence of ionization on temperature (cf. 5.2.1) and the relation between positive *cation-interference* and ionization (cf. Sect. 4), it follows that cation-interference based on ionization will be the more pronounced in the hotter flames. An example is found in STUMPF's report [5]. Cooler flames are often recommended in the literature for this reason.

From the dependence of the dissociation on the temperature (cf. 5.2.1), it is expected that, e.g., interference caused by the formation of chlorides in the flame will be less important in flames of higher temperature. The results plotted in Fig. 3, which were obtained with three flames of different temperature, are in accordance with this expectation.

In order to enable conclusions to be drawn about the formation of alkali chlorides in the flame upon adding HCl to the sprayed solution, allowance should be made for the (depressing) effect of HCl on the sprayer performance. The latter (unknown) effect can be eliminated by plotting the reciprocal of the potassium deflection in relative measure minus the reciprocal of the sodium deflection in relative measure, against the molar HCl content of the solution. When plotted double-logarithmically, a rectilinear curve with slope = 45° is expected, the position

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of which is determined by the extent of alkali chloride formation in the flame only, independently of the effect of HCl on the sprayer performance (cf., for more general discussion, reference [4] p. 161).

Something should be said in this connection about a *special kind of interference* that seems to arise when components such as aluminium, phosphate etc., are added to a solution of earth-alkaline salts. This interference, which may result in a considerable suppression of the light emitted by the earth-alkaline element, appears to be based on the formation of molecular compounds which are either difficult to evaporate (as argued by SCHUHKNECHT *et al.* [23], by MARGOSHES *et al.* [24] and by BERNSTEIN [33]), or difficult to dissociate (as argued by HULDT [25] and by BOITEUX [6]). It may be pointed out here, that not only the degree of dissociation increases rapidly with temperature, but also the evaporation speed of the compound in the solid state increases exponentially with temperature, according to a formula given by LANGMUIR [26].

NOEBELS [27] found, indeed, the influence of sulphate on calcium to be smaller in an oxygen-hydrogen flame than in a cooler air-hydrogen flame. However, when working with three different flame photometers, STRASHEIM *et al.* [28] found no correlation between flame temperature and the observed effect of phosphorus on calcium. It should be noted that in the latter case different flames were used in combination with *different* sprayers, whereas the effect under discussion might depend also on the sprayer performance (diameter of spray droplets, etc.).

5.2.3. In hotter flames often a larger concave *curvature of the calibration curve* is found. The explanation will be clear from what has been said before about ionization, and its effect on the curvature (cf. Sect. 4 and 5.2.1).

5.3.1. Something should be said about the relations between the *dimensions* of the cross-section of the flame, the absolute *emission power*, as defined before, and the *effective light flux* that actually reaches the photocell.

Distinction should be made first between a monochromator and a transmission filter as means for spectral selection. With a given monochromator, the surface brightness of the flame, introduced before as a measure for the absolute emission power, unambiguously determines the light flux that passes the entrance slit. This holds because the dimensions of the entrance slit are usually small as compared with the flame dimensions. This does *not* hold, however, when a transmission filter is used, because here the dimensions of the photocell which are usually comparable to the flame dimensions, enter into the problem.

Let us assume that in the case of a transmission filter a lens is used for imaging the flame, or a part of it, on a cell with a square window, and that the filter dimensions exceed those of the cell, so that the former are not relevant. For reasons of simplicity it is supposed that the flame has a rectangular cross-section. Here the effective light flux is not unambiguously determined by the absolute emission power of the flame, but also the positioning of flame, lens and cell should be allowed for. It can easily be shown, that there is an optimum position that yields maximum light flux on the cell. In this optimum position the magnification factor equals unity, if the flame width is less than the width of the cell opening, and it equals the ratio of cell width to flame width in the opposite case (cf. reference [4], p. 83).

The effective light flux in dependence on the flame dimensions can be calculated, under the assumption that there is no self-absorption, and that flame, lens and cell

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are arranged in optimum position. Here, some general conclusions will be mentioned only.

Since it may be always possible to change the cross-sectional dimensions of a flame at the condition of constant area, by designing another burner grid, it is logical to decide the optimum cross-section dimensions at fixed cross-section area. Under the conditions just mentioned, it appears that, in order to get maximum effective light flux, the flame width should be equal to or smaller than the width of the cell window used. Under this condition the light flux on the cell is proportional to the flame cross-section area only, and does not depend explicitly on flame width, flame depth (or flame length).

So it may now be established as a general rule, that in order to get maximum effective light output with a filter instrument and no self-absorption, one should make:

(1) the cross-sectional area as large as possible (at fixed air supply);
(2) the flame width equal to, or smaller than the width of the cell to be used;
(3) the magnification factor of the optical system equal to unity.

The only, rather obvious rule that holds for a monochromator instrument, requires that the flame depth should be as large as possible.

The limitations that will be set in practice to a large cross-sectional area, at constant air flow, will not be discussed here.

5.3.2. In addition to the second rule just given, it may be said that one should preferably make the flame width not much smaller than the maximum value permitted, so that the flame depth will be as small as permitted. A small flame depth is favourable, as this will reduce the *curvature* in the calibration curve due to self-absorption, in a fixed range of solution concentrations.

5.4.1. The *dilution factor* is composed of the thermal expansion factor and of the ratio in mole numbers of the unburnt and burnt mixture. The former is by far the more important in determining the total elemental content in the flame and the correlated absolute emission power. It has no influence, however, on the line-to-background ratio, in so far as this ratio is determined by the proportion of the two emitting species. The latter proportion is determined by the mole number of the background emitter produced per mole air and the amount of element supplied per mole air.

6. Some general remarks and conclusions

6.1. When an *internal standard*, for example: lithium, is used, variations in flame temperature will—in general—not be fully balanced, because of differences between the internal standard and the analysed element with respect to the ionization and excitation potential and with respect to their affinity for molecule formation. The tendency of lithium to form hydroxide (cf. 5.1.1) should be noted in this connection. Nonproportionality between flame emission and flame content may cause that—in general—also variations in sprayer performance will not be fully compensated.

6.2. In order to reduce *ionization effects*, cool flames or flames that produce an excess of free electrons, are recommended (cf. 5.2.2 and 5.1.1). In the latter case measurements should be made just above the combustion cones, where the content

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of flame electrons may be maximum (cf. 5.1.1). A further investigation into the occurrence of flame electrons would be desirable in this connection. At this investigation a combination of electrical and optical methods of observation is to be preferred. Also the formation of negative flame ions, as established by SMITH and SUGDEN [10], should be studied more closely with respect to its effects in flame photometry.

6.3. Flames containing *hydrogen* are advantageous when an interference due to the formation of halides is feared (cf. 5.1.2).

6.4. The same typical ionization effects described may be expected, when an element is analysed by the *band emission* of its oxides, as when it is analysed by the line emission of its atoms, also if ionization occurs with the atoms only (cf. reference [14]). This holds because of the approximately constant proportion between the atomic content [A] and molecular flame content [AO] according to the law of mass action. Since oxygen is present in comparatively large excess ($[O] \gg [AO]$), one has $[A]/[AO] = C/[O] = $ constant.

6.5. Where there exists some ambiguity about the cause of an effect observed in flame photometry, it is—in general—recommended to make checking measurements with solution contents in the straight as well as in the curved part of the calibration curve, and to make measurements with spectral lines of noticeably different excitation potential, and with elements of noticeably different ionization potential or tendency to molecule formation. In this way it may be decided whether the origin of the effect lies in the *flame* or in the *sprayer*, whether it is related with a variation in flame *temperature* or in flame *content*.

If this method of observation would be applied more systematically, whenever an unknown effect is noted, then the understanding of flame photometry would profit to a still greater extent by the experience acquired in daily practice.

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