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CHEMICAL ANALYSIS OF WRITING IN INK

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CHEMICAL ANALYSIS OF WRITING IN INK

Following is a translation of an article by K. Koopmans in Chemisch Weekblad (Chemical Weekly), No. 55, The Netherlands, 1959, pp. 109-114.

Note: A method is described for comparative chemical analysis of writing in ink in which, by means of photometric determination of the paper, data concerning the quantitative composition of the ink used may be obtained. This form of analysis is a development of the existing, generally used qualitative-chemical analysis of writing in ink.

I. Introduction

The analysis of ink is regularly part of the task of the forensic chemist. It is seldom the case that the original fluid form of the ink is investigated. For the most part the ink is investigated in the form of writing. The question then is whether the inks of various manuscripts are or are not alike, or whether additions or changes in a manuscript have been made with the same ink as that in which the original script is written. Also in cases in which it must be determined whether an inkscript can be produced by a given ink which is in possession of the suspect, it can best be done by a comparative analysis of inkscripts, for which an inkscript is produced (by the investigator himself) with the available ink.

As a rule one has at the most only an extremely limited quantity of ink at one's disposal, and it is also the case that the documents, as important pieces of evidence, should not be damaged, or, at least, as little as possible.

This means that the methods to be used should be such as to derive sufficient information concerning characteristics and composition from a few micrograms of the inks to be compared, so that a conclusion concerning their similarity or dissimilarity may be drawn.

The general methods used so far have only a qualitative character and therefore permit no definitive conclusion.

The following will describe a method developed in the Judicial Laboratory Gerechtelijk Laboratorium with which is shown the possibility of introducing as criteria both the concentration of single constituents of ink, as well as the relationships of their concentrations.

2. Usual methods of analysis of ink on documents

2.1 Visual analysis

After the document, or the part of it to be analyzed, has been photographed in order to record its original condition, there follows a visual examination, both with the naked eye and with the help of a binocular loupe ($V = 10 - 25$ times). Comparison is made of the colors of the inks under analysis and attention is given to the structure of the ink lines. There is seldom a conclusion to be made from the visual review of the color of two ink strokes. The color depends on age, background, lighting, and thickness of the ink layer, and this may result in similar inks presenting completely different colors or tints to the eye. The structure of the strokes is of importance in connection with the question of whether or not the portions to be compared have been made with the same pen. From the structure, also it may be determined whether or not a ball point pen has been used.

Next, documents are studied under ultra-violet or infra-red light. This brings possible erasures to light, while the inks can now and then be distinguished.

2.2 Qualitative chemical analysis (1)

In an analysis of this kind it is usual to put a small drop of a reagent on an ink stroke by means of a very fine glass capillary tube and to study the reaction with the aid of a binocular loupe. Generally use is made of single inorganic and organic acids (hydrochloric, acetic, oxalic and tartaric acids), one or more base reagents (caustic soda and ammonia), an oxidation agent (sodium hypochlorite), a reducing agent (saturated solution of sulfur dioxide), single reagents for iron (yellow potassium ferrocyanide and potassium rhodanide) and possibly reagents for other metals. In this way, one can, however, only make distinctions between inks prepared according to basically differing recipes, such as the following (among which are some which at present are probably no longer used, but which may still be important for forensic analysis); iron-gallnut inks, both with and without blue organic dyes; inks containing carbon; "ball point" pastes; campechechrome and copper inks; nigrosine inks; inks which consist only of a watery solution of a dye (so-called "washable" inks).

If two ink strokes show an evident difference in makeup with reference to one or more of these reagents, it may be concluded that they are inks of dissimilar origin. Here the restriction must be made that there can be no very great difference in their age and in the size of the ink deposit in the stroke. If in analysis, identical behavior is observed, this still does not mean that the inkscripts are made with the same ink (i.e. of the same brand or from the same inkwell), but, at the most, that they are of the same sort. In most cases at law one meets with instances in which no difference can be determined by this qualitative chemical method. The reason for this rests in the inks themselves,

since they, even when they are of different make, show no characteristic differences. On the other hand, the methods applied are not sufficiently sensitive and (or) are not specific enough.

2.3 Chromatographic analysis (2)

Chromatographic analysis of ink, which has rapidly come into use in the past few years, can be applied to ink in the fluid form as well as to ink script.

In this form of analysis one still finds some difficulty in the removal of the ink from the paper fibers. It is difficult to transfer the ink in its entirety to the chromatography paper. The use of a scalpel to shave off a portion and the transfer of the fibers to the chromatography paper is, especially for the thinner sorts of paper, a rather inelegant method. The dissolving of the ink by means of a tested salt solution or organic solvent, in order to make a chromatogram with this solution, is frequently unsatisfactory, especially with old ink scripts.

A second difficulty usually rests in the very limited quantity of ink script which is available for analysis. It should be remembered that on an average about 80 to 100 micrograms of ink is needed for the writing of a single letter of the alphabet so that the quantity of dyestuff per letter is not more than 0.3 to 0.4 micrograms. The quantity of other single components, such as iron, sulfate, and chloride is also of this order (0.3, 0.5, and 0.1 to 0.2 micrograms respectively). It is then evident that one must, on the average, have available the ink in about five letters in order to make a clear chromatograph. As noted above, in many cases such a quantity of ink is not available.

It is evident in these analyses that inks of varying brands, which have entirely the same color to the eye, can provide differing chromatograms. However, different inks can give the same chromatograms, so that, as is the case with the qualitative chemical method, they may not be considered similar inks (because of a similarity of the chromatograms,) without further evidence.

Particularly good results are attained with the ink pastes of ball point pens, and with script from these pens, provided one has sufficient material (4 to 5 letters) available in such a case. In such ink pastes there is generally a combination of single dyes which can be characteristic of a given ink.

Sometimes electrochromatographic methods are applied to the analysis of inks (3). During chromatographic separation in a given direction, electrophoresis takes place in another direction. Possibly this procedure is an improvement, but it is subject to restrictions similar to those noted above.

2.4 Spectro-photometric analysis

If the composition of the ink in its original fluid form is to be analyzed, which can be done only once after determination of the acidity and the concentration of given components, a spectro-photometric investigation may be considered.

As is the case with the methods mentioned earlier, inks of differing brands seem to have both clearly different, as well as practically identical, spectra.

In the Judicial Laboratory the possibility has been investigated of making spectro-photometric analyses of ink strokes on paper, made transparent for this purpose. It seems possible to differentiate among given inks on the basis of spectra so obtained. The spectrum of such an ink stroke shows definite variations from that obtained from a water solution in a cuvet, which is to be expected.

3. Semi-quantitative analysis on paper by measurement of light absorption.

3.1 Further analysis of the similarity of two inks, which show no difference in qualitative chemical relationships, must then be based upon determination of the concentration of one or more components. However, the determination of the quantity of one of the components in an ink stroke has no significance for comparative analysis since it always varies with the thickness of the line. However, in this case the relationship of quantities of at least two components is an important quantitative factor since it remains constant for the whole ink script.

This principle was first applied by Sannie in 1938. As appears from a notice in *Annales de medecine legale* [*Annals of legal medicine*] of that year, he undertook an analysis of the iron content in campeche-chrome inks.(4) These inks originally contained no iron, but as a result of the acid reaction of the ink, steel pens, formerly more in use than now, were attacked so that the iron content of such a campeche ink in a given inkwell increased with the passage of time through the formation of iron chloride. The iron content in ink scripts from these inks thus showed characteristic differences, and in Sannie's publication it was indicated that use could be made of this in comparative analysis of the origin of these campeche inks.

It should be noted that this is, however, a very specific application, which at present is probably no longer significant. Sannie determined, by means of measurement of light absorption, the relationship between the concentration of the dyestuff and the iron chloride, or at least a magnitude most closely connected with this relationship. For this purpose the light absorption of the black dyestuff in the ink stroke on the paper was first measured. After the iron present in the ink stroke was fixed as prussian blue with yellow prussiate of potash [*potassium ferrocyanide*], there followed an oxidation of the dyestuff to a colorless product, after which the light absorption of the prussian blue was measured. These light absorptions were determined with the aid of a microphotometer. The relationship of absorption, measured at the point

of the maximum opacity, offers a good measurement for the iron content and therefore a given campeche ink can be correctly characterized and differentiated from other campeche-chrome inks.

Without doubt, this work of Sannie concerning the quantitative determination of the components of ink by means of measurement of light absorption makes an important contribution to the analysis of documents.

Starting from this idea developed by Sannie; it seemed useful to us to see how far various commercially obtainable writing inks could be differentiated from one another on the basis of the content of one or more common components.

The investigation which followed was made in the way described above, that is, by photometry of ink lines on paper. While Sannie applied such an analysis only to fortuitous impurities (such as the case of iron in campeche ink) we made these measurements of transmission with reference to original components, iron and sulfate. We were able to determine by this means that, in inks which could not be distinguished by qualitative or chromatographic means, the content of the components varied and that these variations could be measured with sufficient accuracy to make possible a determination by this means of their similarity.

In this analysis the light absorption of the original line was first measured. This color was, in the cases investigated by us, based upon organic dyestuffs mixed with the black color of the iron-complex. Afterwards was measured the light absorption either of the iron present in the ink (converted into prussian blue), or of the sulfate, measured in the form of the brown-black colored lead sulfide.

The relationship of these degrees of absorption seem indeed to be characteristic of a given type of ink.

The method can to some degree be compared with quantitative chemical analysis. Furthermore, very small quantities of the substance on paper can be tested thereby. As a rule this is done on the paper itself by means of photoelectric measurement.

Measurement of light transmission can be done in various ways:

1. light transmission is tested at the point of maximum absorption in the stain under study;(5)
2. the absorption by the whole stain under study is determined in a single operation with the help of a sufficiently broad light slit, the form of which can be adjusted to that of the stain to be measured(6);
3. absorption is determined by means of a narrow beam of light on various equidistant spots in the stain.(7) The galvanometer reading is noted for each position of the beam of light and this, or the transmission value determined from it, is entered in a graph opposite the distance. The calculated optical density is also entered. The curves thus entered on the ordinary or semi-logarithmic graph paper together with the 100% transmission line enclose a certain surface, the area of which can be determined with the aid of a planimeter.

Experimentally the relation between either the optical density measured by methods 1 or 2, or the "transmission surface" determined by method 3 and the quantity of the substance in the area of the ink stain was compiled. These reference curves are generally straight for a given area of concentration.

In connection with the somewhat varying form of the "stain" to be measured in our cases, it was a question whether method 1 or method 3 would be considered best. When, following the third method, the transmission was determined for various spots on the ink line and these entered opposite the distance, a curve was obtained like that given in the figure. This shows that in our case the inkline was especially different, because of characteristic "marginal traces", from the usual spots in chromatography.

As may be seen from the results entered in Table I, the relationship of the areas under the curves obtained according to the third method and entered under S is more reproducible than the relationship of the optic density measured at the point of maximum absorption, and shown under D.

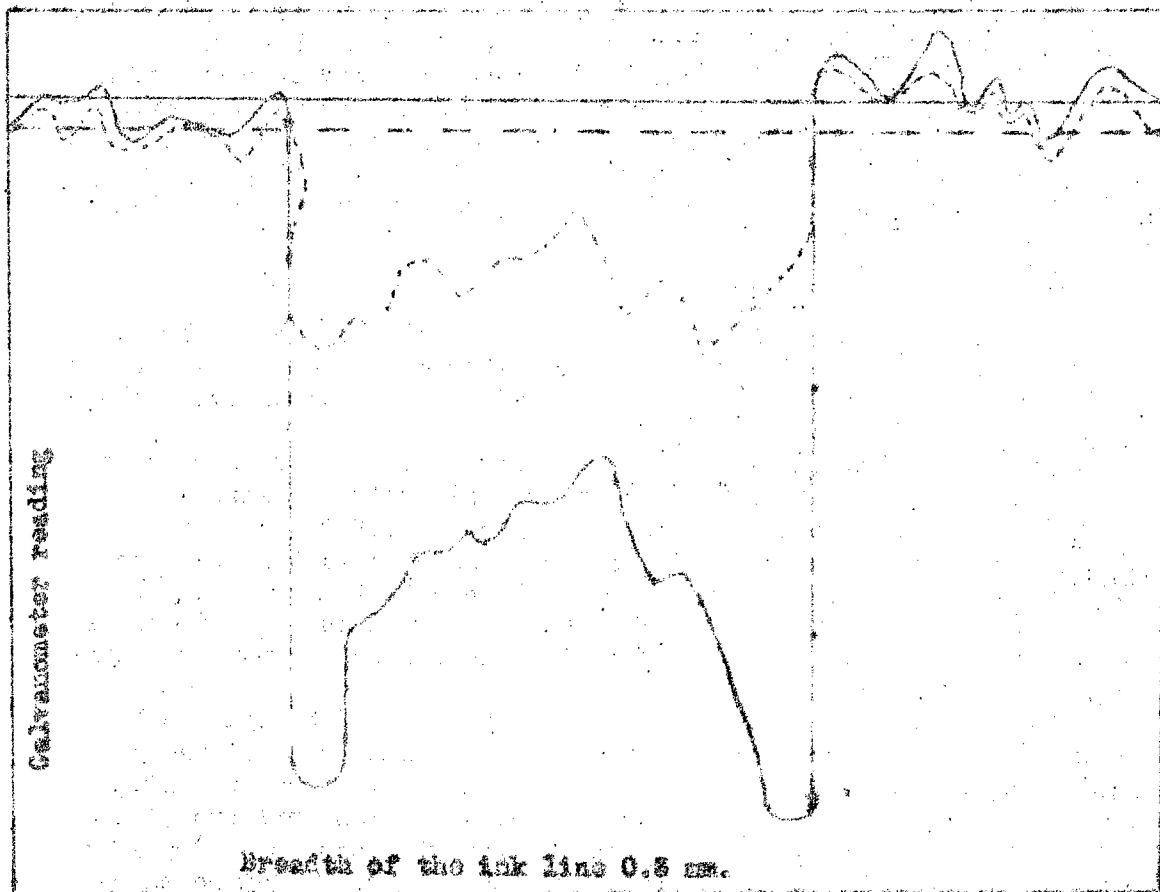
Table I
Comparison of the
relationships S and D
(iron determination)

<u>Ink No.</u>	<u>Tests</u>	<u>Average value of S</u>	<u>Spread in S series</u>	<u>Average value of D</u>	<u>Spread in D series</u>
1	6	0.44	0.41-0.46	0.32	0.27-0.36
2	6	0.87	0.84-0.91	0.68	0.53-0.89
3	6	1.07	1.04-1.13	0.97	0.89-1.10

In general, photometric measurements of colored substances on paper meet with troublesome interferences as a result of lack of homogeneity in the paper. The determination of a quantity of substance of paper can therefore be very inaccurate.

In the determination of the S relationships of the above mentioned surfaces this inaccuracy was to a large part eliminated. This is a result of the fact that first the original ink color and then, on precisely the same spot, one of the ink components -- converted into a suitable compound -- were measured.

It is necessary to make the paper transparent for a measurement of transmission. This is best done through the means of any non-volatile fluid, the index of refraction of which coincides with that of the paper fibers. As did Sannie, we impregnated the paper with benzyl alcohol. A number of other fluids with about the same index of refraction might be used, but their application provides no discernible advantage. In all cases investigated by us it seems that the ink dyestuff absorbed by the paper fiber was not dissolved in treatment with benzyl alcohol.



Legend: ~~-----~~ Ink
 ----- Prussian blue
 Galvanometer reading as function of location, measured along
 the breadth of the ink line.

In general preference is given, in measuring colored stains on paper, to making use of monochromatic light, obtained by filtering a white light. However, the use of white light for photometry has also been successful.(8) In our case we had no great choice. In order to be able to measure such narrow lines of a breadth of from 0.2 to 0.3 mm at various points over their breadth, one must work with a very small light beam and the object to be measured must be moved by means of a micrometer screw. The measurements can therefore best be made with the aid of a microphotometer. Attempts to measure with monochromatic light have failed up till now since the resulting light intensity was entirely unsatisfactory (in connection with the necessary narrow light slit.)

3.2 Making of such determinations and some results.

At a suitable spot in the document a small portion of the script was cut out so that the length of the ink line was about 5 mm. In cases in which a line of such length is not available, a shorter one will do, provided that it is not shorter than 2 mm.

Preferably ink lines are compared with one another in which the quantity of ink per unit of surface is approximately similar.

The area to be analyzed must be so chosen (if there is any possible choice) that the burden of disturbing factors is absent or as small as possible. It should be especially ascertained that the reverse side of the paper is not written or printed upon in that same spot. Also those areas of documents should be avoided which it may be assumed have been frequently handled.

Then the piece is made transparent by means of benzyl alcohol. If this piece of paper is placed in this fluid without previous preparation, it is difficult to make it completely uniformly transparent, since the air bubbles remain attached to the fibers and can influence the transmission of light markedly. Such difficulties can be evaded if the piece of paper is first boiled with petroleum ether, a fact noted by Sannie.

The paper impregnated with benzyl alcohol is fixed between two small glass plates and subjected to a measurement of light transmission. These measurements are made with a microphotometer, according to Hilger. A 10X image of the inkline falls upon the area of the slit which is at a short distance from the photocell. The filament of the light source is precisely focused on this beam. The ink line is then always moved after measurement over a distance equal to 1/10 of the breadth of the slit. In such a fashion 10 to 20 points are measured.

After the original ink line has been measured, the benzyl alcohol is removed with the aid of petroleum ether and, according to the component of the ink to be measured, the iron or sulfate transformed into prussian blue or lead sulfide, respectively.

Conversion of iron into prussian blue is brought about in the following manner:

The iron is fixed by bathing the paper for 10 minutes in a solution of 1 gram $K_4(Fe(CN)_6)$ and 0.75 ml. concentrated H_2SO_4 in 20 ml of water. After rinsing in water for 1 minute, it is placed in a solution of 1 ml 1 N $KMnO_4$ and 0.75 ml concentrated H_2SO_4 in 10 ml of water, so that the organic dyestuff is oxidized and, finally the remaining $KMnO_4$ and MnO_2 are reduced by immersion for 30 seconds in a solution of 1 gram Na_2SO_5 and 0.75 ml concentrated H_2SO_4 in 20 ml water. After rinsing and drying, the treatment with petroleum ether and benzyl alcohol follows, and the transmission of the prussian blue is measured at the identical spot of the original ink line.

The conversion of sulfate into lead sulfide is made in exactly the same way as in analysing the age of an inkscrip.t.(9):

The piece is bathed in a solution of 5% $HClO_4$ and 5% $Pb(ClO_4)_2$ in water. In this process, the sulfate is fixed on the paper as $PbSO_4$. 1% of $KMnO_4$ is added for bleaching the dyestuff in the ink. After oxidation the solution is poured off and the paper is put into water saturated with $PbSO_4$. Afterwards, for bleaching of the remaining $KMnO_4$ and for reduction of the MnO_2 which has been formed, 10% $N_2H_2 \cdot 2HCl$ is added. The paper is then rinsed in water saturated with $PbSO_4$ for ten minutes. After rinsing the paper for a few seconds in 50% alcohol, the piece is transferred to a solution of 1/2 % Na_2S and 1/2 % KOH , by which PbS is formed. Rinsing, drying, etc. follow.

Conversion of iron and (or) sulfate may be done for two inks subject to comparison at the same time and in the same solutions.

The results of comparative analysis of a number of inks by means of a test for iron are compiled in Table II. At the same time the number of tests of each kind of ink, the dispersion of the observation series, and the estimate of standard deviation of the single test are given.

Table II
Tests for Iron

Kind of Ink	No. of Tests	Average value of S	Spread in observations	Standard deviation of single test
1. Gimborn, normal writing ink (old)	6	0.87	0.07	0.027
2. Gimborn, normal writing ink (new)	7	0.75	0.10	0.035
3. Talens, doc. 2001	6	1.07	0.08	0.034
4. Skrip, Shaeffer's 22 perm. blue-black	6	0.44	0.05	0.021
5. Parker Quink solv.x perm. blue	3	0.39	0.02	0.014

Table II (continued)

<u>Kind of Ink</u>	<u>No. of tests</u>	<u>Average value of S</u>	<u>Spread in observations</u>	<u>Standard deviation of single test</u>
6. Talens CC blue-black	3	0.52	0.06	0.027
7. Gimborn, doc. 200. blue black	4	0.31	0.06	0.028
8. Gimborn fountain pen ink no. 290	4	0.44	0.03	0.015
9. Parker Quink solv.x perm. blue black	4	0.50	0.05	0.027
10. Gimborn. 222 diamond blue black	4	0.43	0.03	0.015

In many cases, both relatively thick and thin lines of each kind of ink were measured. The possibility might arise that the relationship of the areas enclosed by the curves (in distinction to the relationship of concentration) may show some dependence on the quantity of ink. Such an agreement between the above mentioned relationship and the quantity of ink has not, however, been found. Thus this relationship remains constant within a given inkscrip, independent of the quantity of ink (naturally referring to quantities which are current for a normal inkscrip.)

Through the joining of similarly varying series of observations, the best estimate for the standard deviation of the single test can be calculated. This is equal to: $S_w = 0.026$ ($n = 37$)

Two inks can therefore be distinguished from each other on the basis of a single test with a statistical certainty of at least 95%, if the difference in the relationship of the surfaces is more than $2 \times 1.4 \times 0.026 = 0.08$.

The results of the comparative analysis of some inks by means of a test for sulfate are summed up in Table III.

Table III
Tests for Sulfate

<u>Kind of Ink</u>	<u>No. of sul- fate tests</u>	<u>Average value of S</u>	<u>Spread in observa- tions</u>	<u>Standard deviation for sin- gle test</u>
Gimborn, foun- tain pen ink no. 290	4	0.51	0.06	0.029
Talens CC blue black	4	0.51	0.07	0.036
Gimborn, docu- mental 200 blue-black	4	0.45	0.14	0.070
Parker quink solv.x, perm. blue black	4	0.30	0.12	0.058
Parker quink solv.x perm. blue	4	0.32	0.10	0.051

Here also the standard deviations and the spread in observations are given.

The best estimate of the standard deviation obtained by a summing up of the similarly varying observations is: $S_w = 0.05$ ($n = 15$). On the basis of a single test, two inks can now be differentiated from one another with a statistical certainty of at least 95%, if the difference in the relations of surfaces is more than 0.14. The standard deviation is in this case about twice that of the test for iron.

In measuring the sulfate there are greater possibilities for variation than in the tests for iron. Many kinds of paper, some of which are very good, contain such a quantity of sulfate that on converting it into lead sulfide, the paper is colored brown.

The sulfate is furthermore less uniformly distributed through the paper, as a result of which the galvanometer reading shows marked fluctuations when the light passes through the white paper.

4. The usefulness of the method for forensic analysis of documents.

As may be seen from the results noted in Tables II and III, the relationship (S) of the surfaces under the curves vary sufficiently among inks and can be determined with sufficient accuracy to make possible an analysis as to whether inks, in the form of inkscript, are identical or not. Thus, for example, Gimborn's normal writing ink can, with the aid of the test for iron, be differentiated from Parker's Quink, permanent blue, with practical accuracy. Above all the iron-gallnut inks, with their relatively high iron content and their wide mutual variations, can be distinguished easily from one another.

The more modern inks generally contain less iron, while the variations in content are less and there are various kinds which have almost the same amount of iron. As a result, some inks, such as Gimborn 222 blue-black and Gimborn 290, cannot be distinguished from one another by this method. However in many cases this method can also be successfully applied to this group of inks.

If an identical S value is found for two inks, it is necessary to apply other methods, such as chromatography. Two inks with an identical, or almost identical S value provide clearly different chromatograms. This is, for example, the case with Parker permanent blue and Gimborn 290. On the other hand, it may happen that two inks with identical chromatograms, have different S values (This seems to be the case with Parker permanent blue and Parker permanent blue black, in which there are variations in the iron content.) The chromatographic and this photometric method can be used either separately in conjunction. The last method may be used with a significantly smaller quantity of material than is needed for making a good chromatogram, which in many cases is an important consideration.

Similar remarks apply to the test for sulfate. In general it is somewhat less usable since there are a number of inks which contain no sulfate, while iron is almost always present.

As noted above, this test is also somewhat less exact. The variation in the content is smaller. That it can nevertheless be of value is shown in case a Parker permanent blue-black ink and a Talens CC blue-black ink are compared with one another. Although these cannot be differentiated as to iron content, this is quite possible by means of a test for sulfate.

In some circumstances these photometric measurements cannot be applied or they are to a more or less serious degree contaminated. This can arise from the fact that the paper itself may contain iron and sulfate. If the concentration is low, which is generally the case with iron, the test can be made with satisfactory accuracy. In addition iron is usually distributed uniformly throughout the paper. The test is more inaccurate, the higher the concentration, and, as noted above, this is often the case with tests for sulfate. The sulfate is less equally distributed in the paper than iron.

The test is very inaccurate when the line is very thin and when the ink also has little iron and (or) sulfate. The variations in the galvanometer readings as a result of light absorption by the substance are then of the same order as the fluctuations in the galvanometer reading as a result of lack of homogeneity in the paper.

As is the rule in forensic analysis, the conclusions can be formulated with more assurance when significant differences in S are found. It should be remembered on this point that two samples of the same make may have different S values, which may be the case if two samples were made at different times and changes in the method of preparation were introduced in the meantime.

The newly developed method should be of particular value whenever the available inkscript is too limited to permit making a chromatogram. In such a case, in addition to a photometric analysis, a qualitative chemical analysis can also be made. If, however, only an extremely limited quantity is available, and if no variations are expected to be shown by a qualitative analysis, -- and this is easy to determine, given some experience -- one can better make immediate application of photometric analysis.

Judicial Laboratory of
the Ministry of
Justice

's-Gravenhage, January 1959.

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