VI.—*On the use of the Prism in qualitative analysis.*

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THE ordinary methods of qualitative analysis depend on a system of exclusion. We first determine that the substance analysed does not contain any member of certain large groups, but consists of one or more members of certain other groups: and these we sub-divide, excluding one division after another, till we arrive at the individual member or members, and these are at length distinctly recognized by special characteristics, or perhaps, special tests. In this process, the indications of colour have hitherto played but a very subordinate part. They have, indeed, been esteemed most valuable when we come to special characteristics or tests, but in any previous stage of the process they are not relied on. Thus, to take an instance:—if, in mineral analysis, we meet with a metal not precipitable by hydrochloric or hydro-sulphuric acids, but thrown down by sulphide of ammonium, as well as by ammonia or potash, as a gelatinous oxide soluble in the fixed alkalis, the green colour of the oxide at once confirms the conclusion that the metal is chromium; but if we see an unknown salt or mixture of salts of a similar green colour, we do not conclude that it contains chromium, nor, if we fail to recognize that colour, do we necessarily infer that chromium is absent. We know indeed on the one hand that there are many other green salts, and on the other hand we speak of some of the salts of chromium as not green, but red, or blue.

Now this arises in a great measure from merely observing the colour as it appears to the untutored and unaided eye. It should be remembered that the colour of an object is the resultant of the various rays of the spectrum which it reflects or transmits, or, perhaps more philosophically, of the various rays which it does not absorb. Yet that colour may be produced by the union of totally different rays; thus—one substance may appear indigo, because it reflects the indigo ray, another, because it reflects the blue with a little red.

This can evidently be determined only by the prism; and in examining the coloured solutions of various salts by that instrument, I have been led to the conviction that chromatic phenomena may be relied on in analysis to an extent, which I think has been

rarely, if ever, suspected. There is this advantage too in such a mode of determining the character of a body, that not a particle of it need be used up in the analysis, nor altered or destroyed by the addition of reagents—a matter of no slight importance when we have to deal with organic compounds, or valuable mineral substances. Mr. Pearsall, and perhaps others, have used the prism with success in particular cases; Professor Stokes has claimed for it a place in the laboratory;* and it is to draw the attention of chemists still more decidedly to this mode of analysis, and to lay down some generalized observations, that I have written the present paper.

The use of the prism is not difficult. Many different methods may be pursued. Professor Stokes examines the chromatic effect of some metallic oxides by fusing them with a bead of micro-cosmic salt, and “viewing through a prism the inverted image of the flame of a candle formed by the bead, the latter being so held as to be seen projected on a dark object.”† In examining a powder or small crystal I have found the following plan answer:—A plate of glass is held in the sun-light in such a position that few, if any, rays are reflected by its surface to the eye, while through it is seen a piece of black cloth or paper in the shade. On the glass is then placed a thin line of the powder, or a small crystal or two, which will of course appear brightly illuminated against a dark ground. By viewing this through a prism, the line of powder will be expanded into a ribbon, or the crystal into a broad image, which, by its varied colours, will show what rays are reflected. Another way of examining a solid substance is by looking at it with a prism through a slit in a black card. But these are inelegant and inexact methods of observation as compared with what is practicable when liquids are examined. We have then to deal especially with transmitted light. The common method is to view by a prism a slit in the window shutter, seen through a glass vessel containing the liquid; but this method generally fails to give intelligible results unless attention be paid to the strength of the solution, and the thickness of the stratum

* Since the above was written, my attention has been called to the fact that Mr. Talbot (*Ed. Journ. Sci.* v, 77, and *Phil Mag.* iv, 114, and ix, 3), and Mr. Crookes, have recommended the prism as a means of distinguishing the different flames given by metallic salts; but this plan of procedure, though doubtless very accurate in certain cases, is of limited and difficult application.

† *Phil. Trans.* 1852, p. 522.

through which the ray passes ; for in most cases the different rays of light are not absorbed immediately on their entering a liquid, but when they have penetrated it to a greater or less distance, and they disappear, not suddenly, but by becoming gradually fainter and fainter. Hence, for holding the solution, I am in the habit of employing, not a vessel with parallel sides, but a hollow wedge of glass held in such a position that the slit in the window-shutter is seen traversing various thicknesses of the liquid from the thinnest possible film to a stratum of perhaps three-quarters of an inch in thickness. This line of coloured light does not then appear uniform : as will be at once foreseen, it varies in intensity from almost pure white to a deep shade ; and it frequently displays variations of a much more unexpected character, being of a totally different colour in one part to what it is in the other ; for instance, blue at one end of the line, and red at the other, every shade of purple intervening. When this coloured line of light is analysed by a prism, very remarkable appearances often present themselves : the whitish portion of the line, where the light traverses very little liquid, will be expanded into a ribbon, differing but little from the spectrum given by unaltered light ; but as the line is viewed through deeper and deeper portions of liquid, some rays are seen to diminish in intensity, others gradually to die out, while others, again, almost immediately disappear, giving place to perfect darkness. If the prism be a tolerably good one, the slit narrow, and the day not too dull, the most visible of "Fraunhofer's lines" will be readily seen running like black threads along this coloured ribbon, and serving to mark with perfect accuracy what rays are transmitted, and what absorbed. The appearances thus presented to the eye can be easily transferred to paper, thus giving at one glance the optical character of the rays which penetrate every different thickness of the solution.

From the numerous observations I have made in this manner, it may be laid down as a general rule that *all the compounds of a particular base, or acid, have the same effect on the rays of light.* Occasionally, but very rarely, a glaring exception occurs ; and much more frequently there are certain variations in degree—the same rays being absorbed, but to a slightly different extent, as compared with one another.

This truth has been partially recognized for a long time : thus every chemist knows that the salts of nickel are green, and those of zinc colourless ; but there are other cases in which it is not so

evident—in fact, where apparent exceptions occur. Some of these anomalies are here discussed.

Chromium Salts.—It has been already stated that some salts of chromium, are called, not green, as the generality are, but red or blue. This remark applies to both solid and dissolved salts. Yet when these various-coloured solutions are examined in the way described above, they all give the same, or very nearly the same, spectrum, and that a very characteristic one. See Fig. 1. The thinnest stratum of liquid suffices to cut off all the yellow rays, and nearly all the indigo and violet: as the thickness increases, the transmitted light appears more and more concentrated about two points, the one at the least refrangible end of the spectrum, the other between the lines *F* and *b*. It is there of a bluish green tint, and is at first supported on either side (if such an expression may be allowed) by blue and by yellowish green, which, however, soon disappear, leaving it also gradually to be absorbed, while the red, which was at first accompanied by orange, passes through the deep liquid alone, and with almost undiminished brilliancy.

The result of this great penetrating power of the red ray as compared with the green and blue, is, that the chloride, nitrate, sulphate, sulphocyanide, and other salts of chromium, which appear green in tolerably dilute solution, appear red when we look through a strong or a very deep solution. This circumstance has been noticed by Schrøtter and others, and has been explained by Sir John Herschel,* who gives the name of dichromatism to the phenomenon. Now the acetate, though it absorbs the same rays as the above-mentioned salts, does not transmit the green so readily; hence it appears usually red, and it is only in very thin or weak solution that it assumes the green appearance: while the “red potassio-oxalate” absorbs the green so speedily that that colour never preponderates, and the thinnest stratum never approaches it nearer than a bluish red. Yet these present a prismatic appearance scarcely distinguishable from that of the salts previously described.

Again, there are two apparently isomeric modifications of some chromium salts, which differ in colour as well as in chemical properties. Thus it is the blue, and not the green sulphate,† that combines with sulphate of potash to form potash

* Ed. Phil. Trans. Vol. ix.

† Berzelius and Schrøtter have both proved this.

chrome alum : but this double salt, though it appears so unlike one of the green compounds to the unaided eye, gives the same peculiar prismatic appearance. The "blue potassio-oxalate," also, though the thinnest stratum of its solution is a faint bluish purple, exhibits the same two maxima of transmission, the only perceptible difference being that the blue space near *F* is very brightly illuminated. An easy method of observing these two modifications is to take an ordinary green solution of nitrate of chromium, divide it into two parts, and boil one of them for a few minutes with an excess of nitric acid. When cool again, the contrast between the two by daylight will be very great, the one a deep green, the other a bluish purple ; but if examined in the way described above, they will present very nearly the same prismatic appearance, the only difference being that the acid solution transmits more light, at least, more of the red and blue rays.

Thus the various chromium salts, though optically very different to the unaided eye, present almost exactly the same appearance, and that a very characteristic one, when examined in the manner suggested.

Cobalt Salts.—We are accustomed to speak of blue and red salts of cobalt ; but this difference depends really on the state of hydration, and the prism reveals an analogy, otherwise unsuspected, between the two colours.

The chloride, and other salts, when anhydrous, are blue. Alcoholic solutions of the chloride, and acetate are also blue.

The chloride, and other salts, when hydrated, whether in the crystallized condition, or actually dissolved in water, are red. The only exception to this, with which I am acquainted, is the sulphocyanide, which crystallizes of a magnificent blue, and gives a saturated aqueous solution, also of a blue colour. The addition of more water, however, gradually changes this to the same red as any other solution of a cobalt salt ; while the subsequent addition of alcohol restores the blue colour to a greater or less degree.

A blue salt of cobalt, such as smalt blue glass, or an alcoholic solution of the chloride, is dichromatic, and if the light reaching the eye has traversed a sufficiently large quantity, it appears red. The alcoholic solution examined in the manner described above, exhibits a very remarkable appearance. It is represented in Fig. 10. The extreme red ray penetrates with the greatest facility, indeed it is much more visible where the stratum is thick, than where it is thin, because in the latter case the neighbouring orange,

by its great luminosity renders it almost imperceptible. Immediately succeeding this narrow red ray, is a thin space of perfect absorption, followed by another red ray, which penetrates a short distance, and by the orange which penetrates a little farther. Then, coincident with the line *D*, but considerably broader, is a space of absolute blackness, while the rays between it and *E* advance far into the liquid, yellow and bright green. The succeeding rays, till near *F*, are greatly reduced in brilliancy on their first entering the liquid, yet they succeed in penetrating it to a considerable distance as a faint bluish green. The blue rays are admitted very readily, the indigo still more so, and the violet advances further yet into the liquid, the lines *F*, *d*, and *G* being very discernible.

A red solution of a cobalt salt gives the appearance represented in Fig. 11. The red and orange rays are transmitted with the greatest ease, the line *D* is strongly marked, the yellow penetrates not quite so far, while the rays between *E* and *F* are very faint, though they are not soon wholly absorbed; the blue passes readily, and the indigo and violet show a constantly increasing power of penetration. The lines *d* and *G* are very distinct.

On comparing the prismatic appearances of these two classes of cobalt salts, it will be at once perceived that both the anhydrous and the hydrated salts transmit the extreme rays of each end of the spectrum most freely. They are analogous also in the faint greenish blue which penetrates for some distance though with but feeble luminosity, between *E* and *F*. Through a strong and deep solution of either the red ray alone passes. There are, however, some equally well marked points of contrast: the orange ray is almost immediately absorbed by the blue salt, but is transmitted with the greatest facility by the red; and the maximum of absorption is, in the one case, about *B*, and in the other about *F*.

Copper Salts.—Anhydrous copper salts present a variety of colours: hydrated crystals, or solutions, are generally blue, but sometimes green; yet the green salts themselves become blue when dissolved in a sufficient amount of water.

Alcoholic solutions not merely of the green chloride, but of the blue acetate, are green. When examined by the prism, they give the appearance delineated in Fig. 5. A thin stratum, even of a very dilute solution, cuts off at once the least refrangible red rays, and the whole of the more refrangible half of the spectrum. The rays from a little before *D* to a little before *F* are transmitted,

and penetrate indeed with almost undiminished luminosity through a very great thickness of solution, appearing to the eye of an almost uniform bright green colour. At first they are accompanied on either side by a little red and blue, but these are soon absorbed. This description applies equally to a saturated aqueous solution of the chloride.

The blue salts of copper, and all aqueous solutions, if sufficiently diluted, give an appearance not differing widely from the normal spectrum. The rays about the blue portion are admitted very freely, while those at each end are partially but not wholly absorbed. They differ considerably in the extent to which these other rays are suppressed; the consequence of which is that solutions of some salts, for instance, the acetate, appear of a much deeper blue than solutions of other copper salts, though of corresponding strength. Fig. 13 is taken from the acetate.

Most, if not all, double salts of copper, (as, for instance, the double sulphate of copper and potash, or ammonia,) are nearly identical with the simple salt both in the character and intensity of the colour. The true ammoniacal salts of copper, which appear so intensely blue, must be distinguished from these, as they appear to contain the copper in some state of combination with the elements of ammonia, and they give a very different prismatic appearance. The maximum of absorption is about *D*, the red and the green rays are transmitted a short distance, while the indigo, violet, and still more refrangible invisible rays, are suffered to pass most freely.

Ferric Salts.—An examination of the various ferric salts is very instructive, in respect to the limits within which there may be diversity in the action of different compounds of the same base on the rays of light. It is well known that they are for the most part red, yet there is an immense difference in the degree of redness exhibited by different salts when dissolved. Thus the nitrate is almost colourless, unless in strong solution; the acetate is vastly redder; while the meconate and sulphocyanide are most intense in their colour. Yet the ferric chloride is orange-yellow, and a solution of the citrate sometimes appears green. In all these cases, however, there is an absorption more or less complete, of all the more refrangible rays, leaving the least refrangible to penetrate almost any thickness without much diminution. This great transmissibility of the red ray causes

those salts which appear of another colour in dilute solution to be dichromatic.

On closer inspection, several groups of ferric salts may be distinguished ; all of which, however, agree in this permanence of the extreme red.

1. Those ferric salts which are red at any thickness, for instance, the sulphocyanide. An extremely thin film, of a strong aqueous or alcoholic solution of this compound, permits all the rays of the spectrum to pass ; but suddenly all are cut off except those less refrangible than the line *D*, and after awhile the extreme red alone penetrates. See Fig. 14. If a weaker solution of ferric sulphocyanide be examined, there will be observed a tendency of the blue ray to manifest itself ; for this salt, as is well known, is altered by the addition of water. See Fig. 15.

2. Solutions of the ferric chloride and citrate give the same prismatic spectrum, at least as far as configuration is concerned, though they appear very different to the unaided eye. The chloride is of an orange-yellow, and whether the solution be strong or weak, deep or shallow, it appears of very nearly the same tint and depth of shade. The citrate, on the contrary, if little be presented to the eye at once, is green ; if more, it is warm brown ; if still more, red. In each case the prism shows that all the rays, from the least refrangible to *E* are freely transmitted ; at *b* the blue begins to fringe the green, but it is soon absorbed ; while every ray beyond that is cut off absolutely, the violet by even a thin stratum of a very dilute solution. See Fig. 6. There is a difference, as will be anticipated, between the intensity of the rays transmitted by these two salts : the chloride admits the orange and yellow to almost any distance with apparently undiminished luminosity ; while the citrate transmits the green rays, subduing the intensity of the others to such a degree that the yellow space at least appears green also.

3. The compounds of ferric oxide with meconic acid and its derivatives form a very distinct group. The *meconate* itself is dichromatic, appearing red *en masse*, but of a peach-blossom colour when in a very thin stratum. The prismatic appearance is given in Fig. 16. The red and orange rays are transmitted freely, the yellow and green are rather soon absorbed ; about *F* no ray whatever enters the solution, but the more refrangible are admitted, gradually fade, and disappear all at about the same distance, and

rather abruptly. The *comenate* of iron gives a prismatic appearance which is almost identical, see Fig. 17; but the more refrangible half of the spectrum is not so luminous, I think; and the indigo ray penetrates farther than its neighbours. The maximum of absorption is about half way between *b* and *F*. The ferric *pyromeconate* appeared indistinguishable by the prism from the *comenate*. There are two compounds of comenamic acid and ferric oxide, the one affording an intense red, the other a still more intense purple solution. Yet different as these are to the unaided eye, they give the same configuration of spectrum when examined with a prism, and this configuration differs from that of the *comenate*, only in the same manner as the latter differs from that of the *meconate*. It is represented in Fig. 18. The *acid comenamate*, which is red, transmits the red, orange, green, and blue, as its congeners do, but allows the violet to penetrate farther even than the indigo. The *basic comenamate*, which is blue-purple in thin, and red-purple in thick stratum, transmits the same rays as the acid salt; but the luminosity of the more refrangible half of the prismatic appearance is much greater, and it penetrates farther.

The ferric gallate, ferrocyanide, and ferridcyanide are perfectly different to other salts of the same base in their action on the rays of light.

Chromates.—It is well known that chromic acid and its compounds are all highly coloured, but that the colour is not the same in all cases; yet the prism, while it indicates a perfect difference between the compounds of chromic oxide and those of chromic acid, exhibits a close analogy between the various chromates. Thus bichromate of potash is red, while the neutral chromate is yellow; but a glance at Figs. 19, 20, will show that their prismatic appearances bear a certain analogy. The red salt in thin stratum permits the least refrangible half of the spectrum to pass, but cuts off at once every ray more refrangible than *F*; as the stratum of liquid increases, it absorbs the slight amount of blue, and the red also, until nothing is visible except a bright band of orange and yellowish green, extending equal distances on each side of *D*, but not quite including either *B* or *E*. The yellow salt admits a somewhat wider spectrum: as seen through the hollow wedge, it presents an uniform band of light, extending the whole length, and consisting of the ordinary spectrum as com-

prized between A and F ; only when it is very thin a little more blue and red appear.

Both chromic acid, and bichromate of silver, though red in the solid state, give orange-yellow solutions, and prismatic appearances almost identical with that presented by yellow chromate of potash.

Litmus.—As an instance from the organic world, litmus may be selected. Every tyro in chemistry is familiar with the fact that this substance is blue when neutral, more blue when alkaline, red when acid, and of a peculiar wine-red colour when affected by either carbonic or boracic acid. Now the prismatic appearances, presented by these differently coloured kinds of litmus, are only modifications of a common type.

If a neutral solution of litmus be placed in the hollow wedge, its dichromatic character becomes at once evident: the thin portion appears blue, the thick portion red, while every shade of purple intervenes. If a line of light passing through these various thicknesses be examined by a prism, it shows that the red penetrates any distance almost unchanged, that the orange is more readily absorbed, that the rays a little less refrangible than D are absolutely stopped, that the green is transmitted to a considerable distance, and is very luminous, that the blue is transmitted not quite so far, and the indigo and violet are still more quickly absorbed. See Fig. 21. If to this solution of litmus, an alkali, whether fixed or volatile, be added, the passage of the red, yellow, green, and violet rays is little, if at all, affected, but the liquid becomes more opaque to the orange ray, and far more transparent to the blue and indigo. See Fig. 22. The extent to which this alteration takes place depends on the amount of alkali present. If to the solution of neutral litmus, boracic acid be added, it manifests its presence by causing the indigo and violet to be more freely transmitted than even the blue, but besides this it produces little change. See Fig. 23. If, however, an ordinary acid be mixed with the litmus, a more extensive alteration is effected: the maximum of absorption takes place not in the yellow, but in the bluish green space, about midway between b and F : the red and orange rays are transmitted with the greatest readiness, the yellow less readily, the green is speedily absorbed, while the blue, indigo, and violet, though faint, penetrate some distance into the liquid. See Fig. 24. The transparency of this solution to the more refrangible part of the spectrum depends

on its degree of acidity; indeed, if very slightly acid, a thin stratum of litmus appears of a light bluish purple.

Salts, each constituent of which is coloured.—When two bodies combine, each of which exerts an influence, and a different influence, on the rays of the spectrum, it might be expected at the first thought that the resulting colour would be the colour of the first constituent, plus the colour of the second constituent; but a moment's reflection will show that this cannot be: the one constituent will absorb certain rays, and the other certain other rays, and the salt itself will transmit only those rays which are not absorbed by either, or in other words, those rays which are transmitted by both. Thus the resulting colour may sometimes to the unaided eye bear no kind of relation to the original colours. As an instance, acid chromate of chromium may be taken. This salt, compounded of two substances which give respectively yellow and green solutions, is not a bright green, but a brownish red: yet this is just what theory requires, as will be evident on noticing the rays not absorbed by either Fig. 1 or 19. And even where the combination of the two substances does give the reputed resultant of the two original colours, as in the chromate of copper (Fig. 9), which is yellowish green, the resulting colour really does not contain the whole of either of the original prominent tints, but is due to the rays that lie between them, and are common to both. Compare Figs. 13 and 19.

This persistence of the chromatic effect of substances with whatever they are combined, renders it sometimes impossible to decide whether two coloured constituents have combined or not; thus, on mixing permanganate of potash with ferric chloride, we still see the very remarkable series of bands that characterizes the first of these solutions (Fig. 12), and the complete absorption of the blue caused by the second (Fig. 6), but there is nothing in this circumstance, either to prove or disprove the formation of permanganate of iron. Nor does the fact that the mixture of the blue permanganate with the yellow ferric salt, has produced a red solution, afford any indication of a chemical change; that colour might be, and indeed was, anticipated from a consideration of what rays were absorbed by each. Indeed, if blue sulphindigotate of potash be mixed with yellow chromate of potash, the resulting colour is likewise red, and not green, although certainly no combination has taken place between them. How easily might a chemist be

misled, and suppose that the unexpected colour indicated the production of a new substance !

This examination of apparent exceptions to the general rule that "all the compounds of a particular base, or acid, have the same effect on the rays of light," shows that, even in these cases, the rule still holds good, or at least that the differences are only modifications of a common type.

The following conclusions, of practical value in analysis may be drawn :

1. When the light transmitted by a coloured solution of unknown composition is examined by a prism, little can be inferred from the fact that a particular ray is absorbed, unless, indeed, we happen to recognize some of those very peculiar black bands which characterize certain bodies, as the permanganates ; but from the fact of a particular ray being transmitted, we may conclude as almost certain that none of those bodies which in ordinary combination absorb that ray, are there present in any kind of combination.

2. Beside this negative inference, we may frequently arrive at a positive conclusion. It is a rare circumstance that the mere colour of a solution will inform even the most experienced eye of what it is that imparts the colour ; but directly it is examined by the hollow wedge and prism, some familiar spectral appearance may be recognized, which cannot be mistaken, and is at once distinctive. Thus, suppose we have an inorganic salt, which gives a green solution : it may be a compound of nickel, or of protoxide of iron or of uranium, of sesquioxide of chromium, or possibly of copper, of ferric oxide, or of the protoxide of molybdenum, or it may be a ferridcyanide, or a compound salt, such as chromate of copper. True, these greens are not all alike to the unaided eye, but the differences of their character are not easily described or remembered ; but let the prism be applied to them, and they are at once distinguished, and that without losing a drop of the solution. The different appearances are represented side by side in the plate, viz. Figs. 1 to 9.

Fig. 1. A salt of sesquioxide of chromium in weak solution. Already described.

Fig. 2. A salt of nickel. A spectrum in which the extreme ends, the red and violet, are soon cut off, while the whole middle portion is transmitted without change.

Fig. 3. A protosalt of iron after being exposed for a short time to the atmosphere. The pale bluish green solution of a pure ferrous salt admits all the rays freely, but the most refrangible are reduced in intensity.

Fig. 4. A protosalt of uranium. These remarkable absorption bands were pointed out first by Stokes.

Fig. 5. Green chloride of copper. Already described.

Fig. 6. Citrate of the sesquioxide of iron in dilute solution. Already described. It differs from the copper salt principally in the constant presence of the red ray.

Fig. 7. Green chloride of molybdenum. Similar to the chloride of copper, but transmitting red for some distance, and a larger amount of blue.

Fig. 8. A ferridcyanide. The potassium-salt (the only one examined) appears green, except in very deep solution, when it is red: the prismatic appearance of thin strata resembles that of citrate of iron, but afterwards absorption takes place of the rays just beyond *D*, and those more refrangible are gradually absorbed afterwards, till at last the rays between *E* and *b* alone penetrate; then these disappear, and the spectrum between *A* and *D* passes onwards alone.

Fig. 9. Chromate of copper. The yellow and green are constantly transmitted; the red and orange are gradually absorbed; the more refrangible half of the spectrum is cut off at once.

These observations will be sufficient to prove that the varying chromatic phenomena exhibited by different substances, may be taken advantage of in qualitative analysis, to an extent which has been hitherto unappreciated. My remarks have been almost confined to transmitted light; but the phenomena of reflected light offer a similar, and as yet almost unoccupied field of investigation. What I have here marked down must be considered rather as a tentative inquiry, than as a really valuable contribution to our knowledge of the effect of different chemical substances on the rays of light; but should any one be induced to take up the matter systematically, he might easily make such a series of observations, as would furnish data for regular tables of comparison, and the prism would then take its place, as the blow-pipe does now, among the recognized and almost indispensable instruments of the analytical laboratory.