K. KOMÁREK:

NOVÉ PRINCIPY ULTRAMIKROANALYSY PRO CHEMICKÝ VÝZKUM

MUSEJNÍHO MATERIÁLU

NEW METHODS OF ULTRAMICROANALYSIS FOR CHEMICAL

INVESTIGATIONS IN MUSEUMS

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Nové principy ultramikroanalysy pro chemický výzkum musejního materiálu

Новые принципы ультрамикроанализа для химического исследования музейного материала

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Pro kvantitativní stanovení velmi malých množství některých prvků a součástí jsem vypracoval zcela nový pracovní způsob analysy, o němž bylo již dříve (4) stručně referováno v české řeči. Dospěl jsem k němu na podkladě dřívější své práce (2). Při ní k dosahování ekvivalenčního bodu při neutralisaci zásad jsem používal pipety vytažené v tak tenký konec, že kapalina (roztok HJO_3) z něho na vzduchu již sama nevytéká, nýbrž děje se tak teprve po ponoření výtokové špičky pipety do kapaliny. Lze tak dosáhnouti velmi přesně ekvivalenčního bodu i ve zcela malém objemu roztoku. Tohoto principu jsem užil již ke stanovení nepatrných množství vápníku a hořčíku (3), která byla posléze převedena na polarografické stanovení iontu JO_3'.

V této studii je popsán pracovní způsob, při němž roztok v *„prýštivé“ pipetě* obsahuje vedle malého množství účinné látky ještě velmi mnoho úmyslně přimíšené vhodné *látky inertní*, která nemá rušivý vliv na správné stanovení ekvivalenčního bodu a kterou lze posléze přesně určit odměrnou analysou za použití mikrobyrety Bangovy nebo i byrety obyčejné. Zkoumaný roztok se vkládá do kratšího ramene zahnuté *reakční trubice*, která má podobu dýmkovitou (obr. 1 a 2). Sloupeček roztoku se pohybuje stiskováním kaučukové trubice, navlečené na delší konec reakční trubice a uzavřené skelným tělískem. Poměr složky aktivní k pomocné inertní součásti musí být přesně znám, jinak se musí provést ještě srovnávací pokus se známým množstvím hledané součásti. Průchodem sloupečku roztoku zúženou částí v ohybu reakční trubice nastává dokonalé promíchání kapaliny.

Popsaným způsobem lze přesně stanovit kvanta látek v množství jen několika mikrogramů. Byly tak stanoveny: Ag', Cu'', Ca'', Cl', OH' a H'. Potřebná aparatura je naprosto jednoduchá, takže lze ji velmi snadno a rychle zhotovit.

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Для количественного определения весьма малых количеств некоторых элементов и составных частей я разработал совершенно новый метод анализа, о котором уже раньше (4) был подан реферат на чешском языке. Я был приведен к нему на основании своей предыдущей работы (2). При ней я пользовался для достижения эквивалентной точки при нейтрализировании оснований пипеткой, вытянутой в столь тонкий конец, что жидкость (раствор HIO₃) из него на воздухе уже сама не вытекала и начинала вытекать только после погружения оттянутого конца пипетки в жидкость. Таким образом можно достичь с большой точностью эквивалентной точки и в очень малом объеме раствора. Этот принцип я применил же при определении незначительных количеств кальция и магния (3), которые были позже переведены в полярографическое определение иона IO₃′.

В настоящем сообщении описывается способ работы, при котором раствор в «сочащейся» *пипетке* содержит наряду с малым количеством активного вещества еще очень много намеренно прибавленного *инертного вещества,* которое не оказывает нарушающего влияния на правильное определение эквивалентной точки и которое можно впоследствии точно определить посредством объемного анализа с применением микробюретки Банга или обыкновенной бюретки. Испытуемый раствор вносится в короткое плечо согнутой *реакционной трубки* Г — образной формы (рис. 1 и 2). Столбик раствора сдвигается посредством сжимания каучуковой трубки, надетой на более длинный конец реакционной трубки и закрытой стеклянной пробкой. Отношение активной составной части ко вспомогательной инертной части должно быть точно известным, иначе нужно произвести сравнительный опыт с известным количеством искомой составной части. При прохождении столбика раствора суженной частью в изгибе реакционной трубки происходит перемешивание жидкости.

Описанным образом можно точно определить количество веществ, составляющее несколько микрограммов. Так были определены: Ag′, Cu″, Ca″, Cl′, OH′ i H′. Необходимая аппаратура крайне проста, так что ее можно весьма легко и быстро изготовить.

New Methods of Ultramicroanalysis for Chemical Investigations in Museums

I. Introduction

Many of the problems relating to identification and conservation which I have had to solve in the course of my work at the National Museum in Prague have required the use of a specially fine investigation technique, as only very small amounts of material have been available for analysis. Because of the lack of the necessary apparatus for carrying out quantitative microanalyses I have used on the one hand polarography and on the other hand I have attempted to elaborate a new way of making volumetric determinations, by which also amounts of about one micro-

gram of the examined substance can easily be determined. In what follows I deal in general with my new working method, which really falls within the subject of ultramicroanalysis, and I add also some concrete examples of the application of my method. For carrying out the operations involved only very simple utensils are needed such as every worker can easily make for himself. The final volumetric determination is carried out by means of Bang's microburette or even by means of a common burette. For some kinds of determination centrifugation is necessary, for which I used an electrically driven centrifuge.

The whole work which I give in the present communication arose mainly from two circumstances. First of all, in a museum we have as a rule by far not so rich a laboratory equipment at our disposal as in scientific laboratories or in large industrial enterprises, and hence it is desirable to replace the expensive apparatus by a more advantageous improvisation. Secondly, in a museum such special and expensive laboratory apparatus is usually not needed, but nevertheless urgent problems do occur occasionally, and for these one may quite well use as a substitute the method elaborated by me. Though this method is considerably slower than the direct evaluation e. g. with the ultramicroburette, speed is not so urgent a consideration in a museum as e. g. with serial work in factory laboratories. Besides the method elaborated by me has in a certain respect even advantages as compared with methods involving the use of complex, expensive and often not easily acquired ultramicroburettes.

II. Apparatus and Manipulative Technique

I have reported already earlier (2) on my new working method, in which instead of the customary titration the reagent (iodic acid) is added to the solution by means of a simple pipette, without any graduation, but drawn out into so fine a tip that the solution in air does not even to the slightest extent flow out from the pipette. It is only after submersion of the fine capillary orifice below the surface of a liquid that a trickling out of the solution begins to occur. When the pipette is lifted, and its orifice emerges again above the surface, the trickling out ceases immediately. Thus we can obtain with a very small volume of the liquid a very sharp equivalence-point, but the amount of effective reagent added has to be estimated subsequently by a suitable method, e. g. polarographically. When one uses a solution of iodic acid this method is unusually sensitive. I used this method of manipulation with advantage e. g. also for the determination of traces of calcium and magnesium (3) in minerals. The solution is enclosed in a glass tube bent in U-shape, whose one arm is below enlarged in bulb-shape and contains here this solution. Gas bubbles pass through this solution, and thus a good and quick mixing is achieved. Instead of mere air one can use for stirring purposes according to requirement also hydrogen, carbon dioxide, or nitrogen.

For my new method of volumetric determination of traces of substances I retained the use of a pipette drawn out into a fine capillary

tip, but I changed substantially the shape of the vessel for the solution in order to be able to manipulate also quite trifling volumes of solutions. Another major change I introduced was especially that for filling the pipette I used composite solutions instead of simple ones, in which in addition to the effective component proper, used only in great dilution, there is present still another auxiliary substance. This second substance is, on the contrary, in a very considerable concentration, and in the first phase of determination, in approaching the equivalence-point, it is absolutely inert. Only after the end-point is accurately reached the real titration of this auxiliary substance is carried out, from whose amount one can then accurately estimate the amount of effective reagent consumed in reaching the equivalence-point, or still better the quantity of the substance is already determined directly after comparative analysis with a known content of the same substance. As the auxiliary substance is in a very strong concentration in the solution, an ordinary burette is often sufficient for its determination. Thus generally speaking each estimation is divided by the way in which it is done into two phases: into *the accurate determination of the equivalence-point* by means of a capillary pipette (*"trickling pipette"*), and then into the *volumetric determination of the inert component "smuggled"* so to speak into the solution examined in a very great, but accurately known excess.

The method of work just described I elaborated in the summer of 1952, and used it also at once for the solution of some microchemical problems which had urgently to be solved within the scope of the work of the Museum. So far I have given only a brief preliminary report in Czech (4) of my new working method. In the present communication I wish also to dwell on some details which are important for the successful carrying out of the whole procedure. It is especially necessary to give some concrete examples of the practical application of the method and the main principles by which the elaboration of the determination of the further elements and components has to be governed in the cases given.

In order to show concretely the proper purpose and working of my method I shall give preliminarily briefly e. g. the method applied to the quantitative determination of silver traces. In the first phase of estimation the equivalence-point is reached by using an apparatus, described below, in the same way as in V o l h a r d's method, but the solution used of thiocyanate contains additionally a large amount of calcium nitrate, which is, however, quite inert at the reaction. It is not until a faint pink tint persists, i. e. after the equivalence-point is reached, that the solution is transferred to a centrifuge cone, the calcium is then precipitated as oxalate, and after washing the amount of calcium is estimated, usually by means of ordinary titration with permanganate solution. For any given weak solution of thiocyanate with a large excess of calcium nitrate one can then directly fix by a test e. g. with 10 micrograms Ag the ratio between the amount of silver examined and the determined amount of calcium, which is then decisive for the calculation of all further determinations of silver in this way. Thus we can determine

with great accuracy silver also in an amount of only a few micrograms.

The apparatus for carrying out the first phase of estimation, i. e. until the equivalence-point is reached in a very small volume of the solution investigated, is shown in Figs. 1 and 2. As in this procedure vessels (pipettes) are used without any graduation, it cannot be called titration. Originally I put the solution of the necessary reagent (e. g. a minimum of KCNS with a great excess of calcium nitrate) into the solution examined (silver salt with ferric nitrate as indicator) so that the salt solution examined was bubbled with gas (air) in a U-glass tube with a bulb-shaped enlargement as mentioned above (2). From time to time the pipette was submerged with its pointed tip below the surface of the solution until the equivalence-point was permanently reached. Thus the effective solution was added in the form of a kind of short injections. As, however, the solution was sprayed asunder by bubbling, and thus came also above the tip of the pipette whence it could not be washed down any more, and also because it was not possible to use this manipulation (i. e. gas bubbles) for very small quantities of the solution, I desisted from this way of manipulation. Instead I fixed the pipette so that it could not move at all, whereas the solution examined shifted freely, and by its contact took from the capillary orifice of the pipette small quantities of the effective reagent until a visible change of the indicator present.

For the preparation of the pipettes as well as for the preparation of the bent reaction-tubes for holding the solution investigated I used chemically resistant Supremax glass with a very high melting point. Thus a Méker's burner had to be used for bending it. As after the breaking of the tubes, first incised with a crystal of carborundum, their ends remained sharp, they had always to be rounded by fusion in a flame. Originally straight pipettes were used; then I discovered that pipettes bent at a right angle are more advantageous. When their open, broad arm is in a horizontal position, and the thin end turned vertically downwards, then one obtains in them in this position a completely constant velocity of the trickling of the solution as soon as their tip is submerged in the liquid. It is only when the reaction solution in the horizontal tube is already consumed and it remains only in the narrowed vertically placed part that the trickling becomes slower and slower.

The length of the wide part of *the "trickling" capillary pipette* is about 4 cm., the length of the fine capillary tip is about 5 cm. Care has especially to be taken that the tube is drawn into the finest possible tip so that after submergence below the water level no bubbles come out of the thin end even under strong air pressure. As by the quick drawing of the tubing in the strong flame of a Méker's burner we do not achieve a sufficiently great narrowing of the trickling capillary, the capillary tube has to be supplementary drawn out after heating in a strongly slanting (almost vertical) position over the quite insignificant flame of a micro-burner or above the pilot-flame of a Bunsen burner which burns also when the main flame is extinguished. Then the capillary tube is gradually cut at the thin end with a sharp crystal of carborundum and broken off until small air bubbles begin to

emerge under water from the tip when the air is driven strongly with a rubber tubing into the wide end of the pipette. Then only the pipette is bent in a right angle and finally it is moderately rounded by fusion at its wide end.
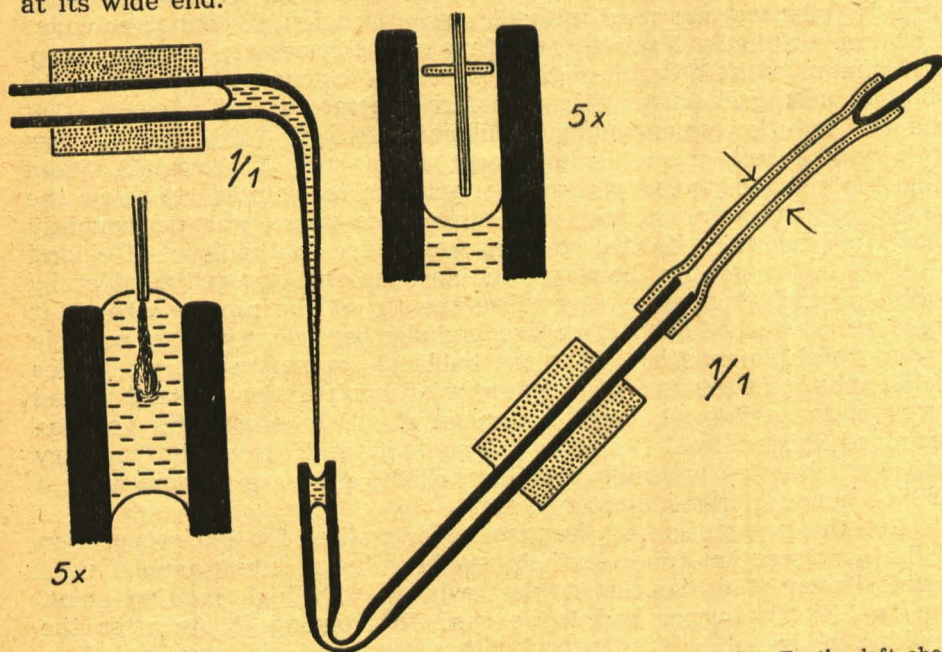

Fig. 1. Arrangement for the determination of the equivalence-point. To the left above is the trickling pipette, to the right below the pipe-shaped reaction tube.

The filling of the capillary pipette is carried ou by attaching a rubber tube to its open wide end, and after submerging the tip of the pipette below the surface of the solution the air within the pipette is thinned through suction by mouth, until the solution rises in the wide arm to a height of about 2 cm. The pipette thus filled can be left lying in a horizontal position, e. g. on a table, also for quite a long time, but its tip must not touch directly what it lies on, especially when it lies on something moist. Thus it must be either gently deviating from the horizontal plane obliquely upwards, or a suitable thin object (a glass rod) is placed under it near its outflow end.

The wide end of the filled pipette need not be closed, as the evaporation of the solution is not accompanied by any disturbing changes, in contradistinction to the simple titration solutions. When some water evaporates from the solution the ratio between the effective and the auxiliary component is not changed at all, so that this evaporation has no influence on the final analytical result. After finishing the work it is best to press out the solution remaining in the pipette through the tip back into the storage vessel if a fairly large amount of it remained in the pipette. In doing so the rubber tube has again to be attached to the wide end of the pipette, and the pressure has to be increased either

only by the mouth or by a rubber bulb for blowing. Before this is done the tip of the pipette has to be washed quickly under a rapid stream of water and then dried by hand (between the tumb and the first finger of the right hand) and wiped several times in the direction towards the end, of course most carefully so that the tip is not broken off. This wiping should be done also immediately after filling the pipette and just before using it, and a thin smear of vaseline on the fingers proves useful for this. Thus it is absolutely prevented that by some chance a tiny drop might form at the orifice of the fine capillary tip in the air, which would spoil the whole work. A tiny drop at the fine capillary orifice of the pipette in the air may easily be formed by a shaking which brings it into contact with its support. Thus at the time of work all shaking has to be avoided.

Still before making the pipette it is desirable to draw a wire with a tuft of moistened cotton wool at the end through the glass tubing in question several times, then to wash the tubing inside several times with water, finally with distilled water, and to leave it to dry. Then only it should be drawn out on one side into a capillary end. It is desirable to have always several ready pipettes in store, as already by a trifling breaking of the end of the tip the pipette becomes often entirely useless as after submersion of the tip in water the solution then trickles too strongly from it.

When the work is finished and the pipette emptied it has still to be washed inside repeatedly either with mere water or also with a diluted acid (after a filling which is hydrolysed by water into insoluble compounds, e. g. into ferric hydroxide), though finally of course again with distilled water. While it is true that it is best when the pipette soon dries inside, even when it is made of chemically rather resistant glass, yet it can be filled without fear with the solution, even when it is moist inside, for the reasons given above. (The concentration of the solution used does not matter, it is only the ratio between its two components which matters, i. e. of the effective substance to the auxiliary accessory substance, for the time inert, admixed in a very great amount.)

If in the solution investigated the estimated constituent is present in an unexpectedly great amount, one uses from the "injection" pipette a relatively large volume of the solution, and for the final volumetric determination of the accessory substance it is better to use instead of Bang's microburette an ordinary burette or a stronger volumetric solution. In order to be able to judge already beforehand which utensils had better be used for the titration at the end of the second phase of estimation, it is well to provide the pipette with an at least approximate graduation for orientation purposes. Then it is enough to mark the volumes only per 0.1 ml., and only in the wide tube from its bend to a distance of about 2 cm., and this can be easily done with a fine file for ampulles or with the sharp edge of a carborundum crystal. This approximate graduation is, however, not necessary, as we can judge the approximate consumption of the reaction solution also from the growth of the volume of the solution in the pipe-like bent reaction tube.

When we know in advance that we shall have a greater amount of the substance investigated we have to use a wider reaction tube (even of more than 3 mm. inner width). In this case it is better when the tip of the pipette reaches into the interior of the reaction tube. For this purpose it is necessary to centre it sufficiently so that its orifice does not get into contact with the moist inner surface of the reaction tube, as this would automatically result in an undesired trickling of the solution from the pipette. The necessary centration can be effected most simply by threading a tiny rubber disc on the tip of the pipette, about 1 cm. from its end (Fig. 1). The disc is most easily made by cutting a slice off a narrow capillary rubber tube with relatively thick walls. When working it is inserted into the orifice of the bent reaction tube. There is no need to insert the pipette too deeply.
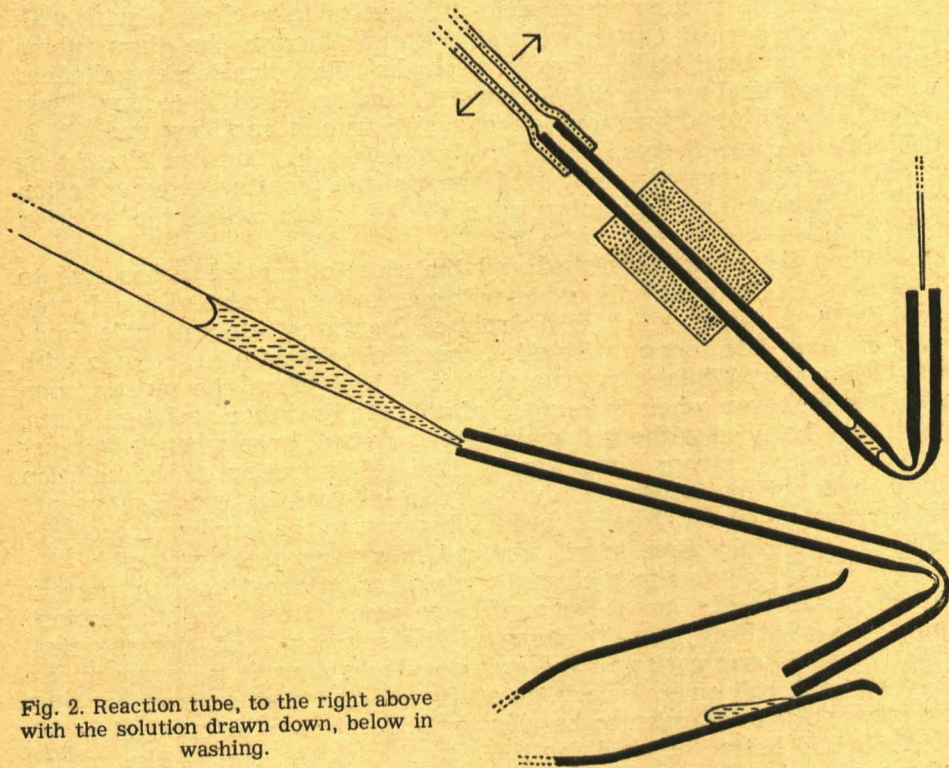

Fig. 2. Reaction tube, to the right above with the solution drawn down, below in washing.

The second main part of the apparatus is the reaction tube (Fig. 1, 2), somewhat like a pipe in shape. For minute quantities of the examined sample in a volume of 0.01—0.02 ml. a tube with an inner diameter of 2 mm. and with a thickness of the walls of 1 mm., of Jena glass was used, as mentioned already above. The length of the liquid column corresponding to the volume of 0.01 ml. is in this tube 3.2 mm. For larger quantities of the examined sample wider tubings have to be used, but their inside diameter must not exceed 3 mm. With an inside

diameter of 4 mm. the liquid column cannot any longer be safely displaced as a whole as it flows slowly into the lower bent part of the tubing so that really two liquid columns are formed, separated by an air bubble.
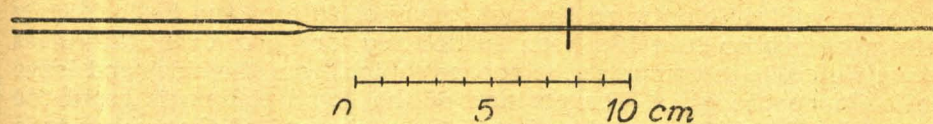

Fig. 3. Thin-walled capillary pipette for introducing the solution examined into the shorter arm of the reaction tube.

The reaction tube is bent under an angle of about 45⁰. With a narrow tubing with an inner diameter of 2 mm. the most favourable length of the shorter arm is about 2 cm., of the longer arm about 6 cm. At the end of the longer arm a piece of rubber tube is put on, which can be closed at its other end by a glass body. The sample of the examined solution is brought into the shorter arm by a thin pipette (Fig. 3) which is emptied by putting a rubber tube, likewise closed with a glass body, on the upper wide end of the pipette. It is good when the tip of the pipette is arcuately bent so that the pipette is not contaminated by the pressed out solution, and so that the solution can be pressed in the direction against the inside glass surfaces of the tube, to which it adheres. The necessary reagents (indicators, acids, etc.) are preferably introduced into the shorter arm already before the solution examined is let into it. For introducing them into the apparatus it is best to use only a glass rod drawn out to a fine point (0.5 mm.) with a tiny glass ball.

Both orifices of the reaction tube have of course to be lightly rounded by flame. Still previous to starting work the circular orifice of the shorter arm has to be slightly smeared with vaseline. This is necessary in order to prevent the solution, which is pressed out to the very end of this arm, from flowing out over the edge, and thus it is at most only vaulted upwards from the orifice of the tube in the form of a hemisphere. It is of course not advisable to press out the solution too high above the edge.

As in some determinations the blank values have to be respected for a certain final volume of the solution, in order to substract them from the result and thus to obtain quite accurate values, it is good when the reaction tube has in its lower part on both sides from the bend an at least approximate calibration scale for every 0.02 ml. This can be made in the same way as described for the trickling pipette. As the tubing is thinnest in the bend, it might be too much damaged in these places by a stronger pressure of the carborundum crystal and break already at a small shock. Thus it is better to begin with the calibration scale to the left and to the right of the bend where the glass is already sufficiently strong.

The filled reaction tube is placed with the short arm vertically upwards. Only after filling with the solution investigated, which settles

in the bent middle part, we attach at the end of the longer arm a rubber tube closed by a glass body and inside sufficiently smeared with vaseline. In doing so its open end has to be strongly compressed from the sides so that the air can stream outwards, for if this is not done, the solution will shift outward through the shorter arm and be lost. Only after the rubber tube has been sufficiently dragged over the glass tube, we cease to compress the rubber tubing from the sides and leave it to lie on the glass. The position of the liquid column is regulated either by the shifting of the glass body at the end of the rubber tube or by the shifting of the rubber tube on the end of the reaction tube. We have to reckon with the fact that by a suitable compression of the rubber tubing we have to move the examined liquid column in the operation to the very orifice of the short arm and back again to the narrowed middle part. For this purpose a sufficiently long rubber tubing has to be chosen. The liquid column is then placed so that with the rubber tubing left free it lies behind the narowing in the lower part of the longer arm.

The trickling pipette is fixed so that its tip (orifice) reaches to the middle of the shorter arm of the reaction tube. Both parts of the apparatus are in a vertical position. The trickling pipette as well as the reaction tube have to be fastened as firmly as possible with metal clamps to the vertical column of the stand. First it is necessary to fix the reaction tube and then above it the pipette. In the final tightening of the screw at the clamp with the trickling pipette the tip of the pipette changes its position very considerably, and there is the danger that it either touches the end of the reaction tube or even breaks by pressing against it. Thus the lowering of the trickling pipette and the tightening of the screw holding it have to be done very carefully, first so that the fine orifice of the capillary pipette is placed after the firm tightening of the screw some millimetres above the middle of the shorter end of the reaction tube, and then only is it shifted vertically downwards and carefully centered so that the orifice of the capillary outlet tube falls accurately into the geometrical centre of the circular orifice of the reaction tube. When using wider reaction tubes (even a little over 3 mm. in inner diameter) a pipette with a rubber disc near the end can be used, which is inserted into the orifice of the reaction tube. As at the end of the procedure it is necessary to rinse with the column of the solution inside also the upper part of the reaction tube in the places above the end of the pipette, it is better to insert the tip of the trickling pipette at first somewhat more deeply and only at the end of the procedure to raise it upwards by about 5 mm. After the equivalence-point has been accurately reached, the tip of the trickling pipette is drawn out completely and removed, the liquid column is then displaced to near the orifice of the reaction tube in order to ascertain whether any change occurs any longer in the appearance of the solution. A gentle smearing of the circular rim with vaseline is necessary also here, so that in emptying the content the solution does not cling to the outer side at the end of the short arm of the reaction tubing, and so that the washing of the whole tube can be carried out perfectly.

After the perfect centration of the tip of the trickling pipette, filled already with the reagent solution, in the orifice of the reaction tube, the column of the solution examined is pressed vertically upwards until it touches the end of the pipette. As soon as it does so the reagent solution begins to trickle in a very fine stream downwards into the solution investigated. As the solution examined is always very diluted, and as on the contrary the reagent solution contains an unusually large amount of auxiliary salt, the reagent solution streams always very quickly downwards, and thus passes easily through the whole column of the solution examined, standing vertically, as far as to its lower end.

The mere trickling of the reagent solution from above downward cannot of course bring about a mixing of the liquid. Therefore it is necessary to loosen the pressure on the rubber tube, by which the liquid column is shifted back into its original position, downwards into the middle of the tubing. As, however, a perfect stirring does not take place until the whole liquid column passes through the narrowed middle part of the tubing to the other side, into the lower part of the longer arm, we have to see to it that this latter position is already at the beginning of the procedure the initial position. For the purpose of the most perfect possible stirring it is of course better when the liquid column is moved in both directions several times consecutively through the narrowed bend of the tubing and then only pressed again upwards, where a further portion of the reagent solution enters it.

As soon as the coloration characteristic in the given case for the reaching of the equivalence-point begins to disappear only slowly in stirring, it is necessary to effect the contact with the fine opening of the hair-tipped capillary always for a very short moment only. It is not until after the end-point has been reached that it is necessary to draw the solution also higher into the longer arm, and thus to wash also the marginal part which the solution column had not reached before. It is probable that this will defer again the end of the procedure as the liquid loses again the coloration characteristic for reaching the equivalence-point in question, and it is then necessary to finish the operation most carefully. In the reaction tube the lower part of the longer arm thus represents a kind of small reserve of the estimated component, which especially with quick and not too careful work may prevent errors resulting from the addition of an excess of the reagent solution greater than is just necessary for reaching the accurate equivalence-point.

For the perfect fixation of the two main parts of the apparatus in the clamps it is necessary to use rubber cylinders or at least rubber stoppers with holes of the appropriate width (Fig. 1). In order that the pieces of rubber may be shifted easily on the glass, it is necessary first to smear them inside with glycerol. Then only both tubings are inserted into the holes, and the surface of the glass, over which the rubber pieces were drawn, are freed of the glycerol as completely as possible with moist filter paper. This has to be done especially well at the orifices of the two tubes, as the glycerol by its ability to form firm complex compounds with many metals might even in traces cause considerable errors in the determination. Or one can insert both tubes into the rubber

cylinders also without coating them with glycerol, provided that the rubber cylinders are cut longitudinally, but only so that on one side they remain connected together to form one whole. For accurate and safe work it is necessary that the rubber pieces with the tubes inserted in them are as firmly as possible clasped by metal clamps lined inside with cork.

It may happen that after pressing the liquid column into the upper part of the shorter arm, the column after a while shifts slowly down by itself, although the rubber tube remains also further equally compressed. This is an indication that the rubber does not tighten well, and thus does not lie well to the glass. If we let the column thus sink for a while and only then release the pressure on the rubber tube, the solution column is displaced via the narrowed middle part unexpectedly far into the long arm. Then it is necessary either to smear the rubber tubing inside with vaseline or to use another tubing which fits closer and has no small fissures.

We have especially to avoid that the liquid column inside the reaction tube tears into two, separated from each other by an air bubble. This may happen e. g. by a too rapid shifting of the solution. It is sometimes rather difficult to reunite the two columns again into one, and it takes a long time, but it must be done is the procedure to be finished. As said above, the imperfect tightening of the rubber may after a certain time cause an unfavourable position of the liquid column. When it is not possible to correct this at once by exchanging the rubber tube, the correct position of the liquid column has to be achieved solely by the suitable pushing in or on the contrary pushing out of the glass body by which the rubber tube is closed at the end. For this closing we can use of course also short glass rods, but quite short glass tubes gradually drawn out towards both ends, which are sealed (Fig. 1), are preferable.

As soon as the equivalence-point is reached the first phase of the whole procedure is terminated. The clamp with the pipe-shaped reaction tube is at once lowered ,and only then is the tube loosened from it and taken out. The solution maintains itself in the bent middle part of the tubing. In this position we place to the orifice of the shorter arm of the reaction tube either a centrifuge cone, a small beaker, or a small Erlenmeyer flask, and then only the whole reaction tube is turned so that the solution from the short arm flows out into the vessel against whose inner wall the orifice of the arm is placed. Then a few drops of distilled water are put with an ordinary glass pipette into the longer arm; the water runs through the bend into the shorter arm and rinses the tubing inside.

Even when the orifice of the short arm of the reaction tube has been coated slightly with vaseline, it is advisable after rinsing the tubing inside to wash also the orifice of the inverted tubing outside with two or three drops of water from the pipette, keeping the tubing constantly in contact with the inner side of the vessel (Fig. 2). After this quantitative removal of the liquid into the vessel there remains only the estimation of the subsidiary component, hitherto inert, which was „smuggled" in a great amount into the liquid in connection with the strongly diluted effective constituent of the reagent solution. This estimation is carried out in various ways according to the accessory salt used. Accordingly we have to decide already in advance on the kind of vessel needed (centrifuge cone, etc.) and also on the corresponding preliminary preparation of the solution. The individual possibilities will be discussed below in connection with the examples given. In some cases one can after a short and easy preparation of the solution pass at once directly to the final volumetric determination of the auxiliary component by means of ordinary burette or Bang's microburette. For a more accurate determination of very small quantities of substances it is best to empty out the volumetric solution very carefully from Bang's microburette, its outlet tube being in direct contact with the humid inside surface of the vessel while quickly stirring the solution in the lower part.

After emptying the content the inside of the reaction tube remains sometimes soiled by an adhering fine precipitate (AgCN, mercuric nitroprusside, etc.). If a complete cleaning cannot be achieved by the use of suitable reagents (ammonia, potassium cyanide, etc.), mechanical cleaning has to be carried out by means of a small tuft of moist cotton wool fixed to the end of a thin wire. This mechanical manner of cleaning cannot be carried out in the thin bent part of the reaction tube, and it is then preferable to use for this purpose a narrow feather, e. g. the pinion of the wing of a partridge. Special care has of course to be taken that the glass inside the trickling pipette or the reaction tube is not greasy, as this would produce disturbing irregularities especially in the movement of the inner liquid filling. There is no need first to dry the moist tubing; it is enough to rinse it twice consecutively with a few drops of acetone or ethanol, by which the water is quickly removed, and only then are the traces of grease inside the tubing removed by rinsing twice with petroleum ether (benzine). The vaporisation of the organic solvent takes place very quickly after attaching the tubing thus purified to a filter pump. As the acetone or ethanol mixes with water as well as with benzine, the procedure here described is the most suitable for the given purpose. Instead of benzine one may use e. g. also carbon disulfide, which likewise mixes well with acetone and also dissolves vaseline excellently. Carbon tetrachloride on the contrary cannot be used instead of benzine for the given purpose, as it evaporates very slowly. The thin coating of vaseline made on purpose at the end of the tubing has to be removed mechanically, at least in its main part, already before using acetone, by means of moist (and therefore soft) filter paper.

When one uses a reaction tube with an inside diameter of more than 2 mm., the procedure is analogous. In the final rinsing of the tubing with water care has to be taken that the inclination of the reaction tube is only small, so that a small amount of water is sufficient for rinsing it; but it has to pass through it slowly. Even if in the work itself (injection of the reagent solution) the liquid column does not rise quite to the orifice of the short end, it is necessary to coat the orifice of the tubing and a narrow outside band below it very slightly with

vaseline so that in the final draining and rinsing not even a little of the solution adheres here needlessly long.

The ratio of the content of the wide arm of the trickling pipette (calculated only for a column about 2 cm. long) to the quite trifling volume of the solution, which trickles out in the short „injection" from the tip of the pipette, is incomparably greater than the ratio between the volume of an ordinary burette (50 ml.) and one drop (0.04 ml.) of the solution. This gives us on the one hand the advantage that the trickling pipette represents even with the rather small part of its wide arm a considerable reserve of the reagent solution, and on the other hand that this solution can be added to the sample examined even in minute amounts.

In precipitation reactions (argentometry, mercurimetry) the fine capillary opening of the trickling pipette is sometimes stopped up, and thus the accuracy of the result may be considerably endangered. If from the considerable rapidity of the reaction it is then evident that the equivalence-point is still very remote, it is enough to attach to the wide end of the trickling pipette a long rubber tubing ending in a glass tube and by sharp blowing to remove the stoppage in a very short time. When, however, it comes to a stoppage already near the equivalence-point, then there remains nothing to be done but to rinse the end of the trickling pipette quickly and carefully with a droplet of distilled water by means of a glass rod drawn out into a fine (0,5 mm. or less) end. This manipulation has to be carried out so that the droplet of water runs down into the orifice of the reaction tube and thus carries along also the main part of the solution adhering to the end of the stopped-up capillary pipette. Then the trickling pipette is lifted upwards, is loosened, and purified by pressure. Then its tip is finely smeared on the sides with vaseline, and the operation can continue.

III. The Chemical Foundation of the New Working Method.

I arrived in a logical way at the working method described in detail in this paper from my way of bases determination (2) mentioned already earlier, whose method is very briefly outlined on p. 20. The final estimation of $IO_3{}'$ I carried out polarographically, and I used this my new method with success immediately for the solution of the problem which arose when calcareous fossils and fine shells in the museum collections fell to pieces in contact with glass. This disturbing phenomenon was caused by the excessive alkalinity of the glass (4), which by the new method could be easily and accurately traced. The main point of the determination is the neutralisation of the extract by iodic acid by means of the trickling pipette.

As also the iodimetric determination of iodates is considerably accurate, I then tried to use instead of polarography for their estimation titration with thiosulfate solution added from a Bang microburette to the starch end point. To increase still more the sensitivity of the determination I added sufficient potassium iodate to the solution of iodic acid. This achieved that for the neutralisation of a slight alkalinity

very much weak acid solution of iodate was used. The content of iodates was then estimated iodimetrically. From the results with known amounts of the base one can estimate accurately from the final consumption of 0.01 N thiosulphate the very small analysed alkalinity. Thus potassium iodate was „smuggled" into the reagent solution proper (iodic acid) in a great amount as a component inert at neutralisation, from whose amount it was, however, possible in the final determination to estimate very accurately the amount of the constituent estimated, here of the base (OH').

Though the principle of my working procedure is essentially fairly simple, many obstacles arose in carrying out the new method in practice. The main problem which had to be solved as satisfactorily as possible was the choice of suitable inactive admixtures added in a strong concentration to the effective constituent proper, which in other methods is used alone without admixtures for titrations. It goes without saying that the auxiliary substance, which can be used in great concentration as admixture to the volumetric solution, has to comply especially with the following demands:

1. It must not react at all with the effective substance, which is the main constituent of the volumetric standard solution.

2. A sufficiently accurate volumetric method, easy to carry out, must exist for its quantitative determination.

3. The compounds which are formed by the reaction of the substance examined with the active substance proper of the reagent solution must not have an adverse effect on the accurate volumetric estimation of the auxiliary substance, which is the final act of the whole work.

Relatively very few substances answer all three of these demands. Further we have to remember that there are not either many volumetric determinations which can be carried out easily and accurately. Already from these two facts it follows that the new method can be used only in some cases, and that the mere apparatus is by no means sufficient for the actual practical application of the method. Thus it is necessary to elaborate for the estimation of each given substance, when using the manipulation procedure described, an entirely new way of determination, in which the first phase of procedure corresponds to the reactions which take place in ordinary titrations, but where the second phase demands sometimes certain special operations in order to eliminate the otherwise disturbing influence of the substances present.

For the first phase of determination come into consideration the common reactions manifesting themselves in titrations. As iodimetric determinations and titrations with permanganate are particularly accurate, it was suitable to use just these for an accurate determination of the equivalence-point. The „trickling" pipette in connection with the use of the „pipe" reaction tube enables us to fix sharply the equivalence-point even for very small volumes of solutions. Thus in the first phase of the procedure it would be suitable to use as reagent solution especially a diluted solution of thiosulfate, iodine or permanganate, which

besides the active component mentioned above would always contain an excess of a suitable inert salt. Only in the second phase of the procedure, when we have to deal with the titration of relatively greater quantities of substances, one can use rather neutralisation or precipitation reactions, even though these are far less sensitive than the oxidation-reduction reactions. These latter are suitable for the first phase of the operation, i. e. for the work with the trickling pipette, because they exclude a stopping up of the capillary outlet, in contradistinction to the precipitation reactions. But the possibility of a choice of the reaction is unfortunately not so great that the method just outlined can be used invariably and easily.

It will be best first to state which salts can be added as an *auxiliary inert substance* to the solution of thiosulfate, iodine or permanganate in the sphere of my working method. Here it is necessary to remember that even when in the neutral or only weakly acid medium itself two given substances are mutually practically entirely inactive, it can come suddenly, after introducing their mixture into the acid solution examined, also to their mutual reaction. In other words, the mutual inactivity of the two may be only apparent, obtaining e. g. only for the neutral reagent solution, but need not be preserved in another medium.

A relatively very suitable inert admixture is afforded by calcium salts. Though calcium cannot be estimated directly, yet it can be precipitated in the second phase of the operation as oxalate, and by centrifugation and washing the amount of calcium oxalate can be determined with a standard solution of permanganate. The advantage of this procedure is that the cation Ca¨ cannot react at all with permanganate, and thus is neutral, and also the acid reagent solution is very stable. It is of course a drawback that it is necessary to precipitate, centrifuge and isolate the calcium oxalate in a pure form, which lengthens the determination. As a calcium salt I used mostly for the given purpose calcium nitrate. Its solubility is very great, so that a specially great ratio of calcium to permanganate, and thus also a great accuracy of the final determination, can be achieved. It is of course necessary to ensure that before the precipitation of the calcium oxalate the solution does not contain any sulfates or phosphates, as in that case the calcium will be prematurely precipitated as an insoluble salt.

In the precipitation of the calcium in the second phase of the procedure care has to be taken to add to the hot acid solution, which contains also a minute amount of manganous salt, ammonium oxalate in sufficient excess, and only then to add ammonia up to a distinctly alkaline reaction. The manganese present is not precipitated at all from the solution, as it is bound in it in the form of a soluble complex compound. But even if this were not so the error arising from its presence (as insoluble oxalate) would be eliminated by the amount of manganous salt present being directly proportionate to the amount of „smuggled in" calcium. Thus after essaying with a known (preferably rather large) amount of the constituent to be determined one would calculate for the same reagent solution under observation of the same working

conditions also the accurate content of the component to be determined. Thus it depends mainly only on the component estimated not acting disturbingly in the final determination.

It goes without saying that the solution of the substance investigated must not contain already perhaps beforehand the same component which as inert admixture is in the reagent solution. In the case given it has thus to be free of calcium salts. Similarly cation Ca¨ (in the form of calcium nitrate) can be used as admixture to the solution of thiosulfate or to the iodine solution.

Instead of cation Ca¨ one can use as admixture for the oxidation-reduction reactions also other substances, though as already said above the choice is not great, as they comply only rarely with the demands listed above. Thus e. g. we can use as admixture to potassium permanganate also a saturated solution of sodium chloride, and in the second phase of the procedure the amount of chlorides is estimated most easily by means of mercurimetric titration according to E. Votoček (9), using sodium nitroprusside as indicator. This will still be discussed in greater detail in the section with examples of some estimations.

It might be thought that iodates would be a suitable admixture to a solution of potassium permanganate as they can be determined very easily and very accurately. Unfortunately they cannot be used. Though in a neutral solution they do not react with potassium permanganate, yet as soon as this mixture is introduced into an acid reaction medium (1), the iodate, present there in great excess, would be oxidised at least in part to periodate. Besides in some cases the component estimated, with which the permanganate is to react, could be oxidised already by iodate.

Chlorides of course do not come into consideration at all as auxiliary admixture for iodimetric reactions. When using a solution of iodine one can, however, gain by the new method a very high accuracy of estimation, in those cases where the analysed component proper does not act disturbingly: A small amount of elementary iodine is dissolved in a very strong solution of potassium iodide, and this slightly yellowish brown coloured mixture is then used for filling the trickling pipette. The solution has to be kept in darkness, and its content of free iodine has to be controlled fairly often. After reaching a blue coloration of the investigated liquid (from the presence of starch) the content of the reaction pipe-tube is washed out, and the iodide is transferred by oxidation with saturated bromine water quantitatively in anion IO_3^- (7). The excess of bromine is removed by formic acid (8). Then sufficient KI is added, and the iodic acid formed is estimated iodometrically by means of 0.01 N $Na_2S_2O_3$. This method will be described in detail elsewhere in an another separate chemical article.

In view of the great solubility of KI in the reagent solution and in view of the great sensitivity and accuracy of iodates determination the method described permits a great accuracy of estimation even for quite minute amounts of the substance determined. The procedure is relatively quick, as it does not demand any centrifugation either for separation or for washing purposes. It can be used e. g. for the estimation of

minute quantities of arsenites or arsenic trioxide. Though the very minute amount of arsenates formed is finally titrated together, yet their amount is quite negligible, and besides it is taken into account in the comparative essay with a known quantity of arsenites, and the amount is accurately proportionate to the quantity of smuggled in iodide or of the finally resulting anion of iodates.

The scope of the new investigation method will be enlarged if it proves possible to treat in the first phase of the procedure also precipitates, e. g. calcium oxalate. But here a pipe-tube cannot be used, but only a small centrifuge cone as will be discussed still in the final section with supplements to the general manipulation technique.

For the first phase of procedure with the use of a trickling pipette and a pipe-tube a suitable oxidation-reduction or permanganometric method cannot, however, be applied always. Thus one has to be satisfied for this purpose with the use of the less sensitive neutralisation or precipitation reaction, where it is sometimes even necessary to take corrections for the volume of the examined solution, ascertained by blank determination carried out parallelly.

For estimating minute quantities of *a c i d s* or *b a s e s* a reagent solution can be used which contains in addition to hydroxide or acid still an excess of potassium iodate. After effecting the neutralisation the amount of smuggled-in IO_3' is estimated iodometrically and from the consumption of 0.01 N $Na_2S_2O_3$ the amount of the acid or base in the sample examined can be calculated. The precondition for this is of course the absence in the sample examined of reducing substances which would react with IO_3'. With a very minute amount of the estimated acid or base it is necessary to pay attention to the correction determined by blank determination for the same volume as is the volume resultant after reaching the neutral point. It is also advantageous in terminating the neutralisation by means of the trickling pipette to have in front of one for accurate comparison the colour tone which the indicator gives (e. g. methylorange) with approximately its equal concentration and equal volume in the acid medium and in the neutral and alkaline medium. It is of course also possible to add instead of KIO_3 to the acid or base much $Ca(NO_3)_2$ or $CaCl_2$, and after neutralisation in the pipe-tube to precipitate from the resulting solution calcium as oxalate, and to estimate its amount permanganometrically. The procedure is then, however, considerably lengthened by the necessary centrifugation, and calcium cannot be used as admixture in the case of phosphoric or sulphuric acid because of the little-soluble corresponding salts.

In using an admixture of KIO_3 to the solution of acid for determination of traces of bases the concentration of anion IO_3' is, however, considerably limited on account of the small solubility of acid potassium iodate, whose existence (or, better said, ability to precipitate in solid form) we have to assume in such a solution. Thus the procedure outlined is suited only for the determination of very small amounts of bases (around 1 microgram) as with greater amounts (in using about 0,01 N H', i. e. 0.1 N HIO_3) the volume of the acid mixture added would soon exceed the original volume of the solution examined (0.01—0.03 ml.). On the

other hand, in the determination of small quantities of acids this difficulty does not arise, as the slightly acid solution of potassium iodate can include a far greater amount of IO_3'.

For the determination of *s i l v e r* we can proceed in several different ways, but in the present paper we shall consider only its precipitation with sulfocyanate, where simultaneously a very great amount of calcium salt is introduced into the solution. As indicator we use preferably ferric nitrate (instead of ferric alum). The calcium is then estimated as oxalate, finally by titration with a solution of 0.01 N $KMnO_4$.

For the determination of *c h l o r i d e s* it is advantageous to use the mercurimetric method according to E. Votoček (9), where a great amount of $Fe(NO_3)_3$ is introduced into a small amount of the solution examined. In the second phase of the procedure the amount of $Fe^{...}$ smuggled-in is estimated iodimetrically. When turbidity caused by mercuric nitroprusside begins to appear, the solution is moved from the pipe-tube to a small centrifuge cone, a small crystal of NH_4CNS is added cold, and after stirring $Fe(OH)_3$ is precipitated immediately with ammonia. Then only the cone is heated by placing it in hot water. After centrifugation and rinsing with water $Fe(OH)_3$ is dissolved in 4 N (or weaker) HCl, and the iron is estimated iodimetrically.

L e a d is transferred, after separation from other metals and precipitation as $PbSO_4$, with silver chromate into insoluble lead chromate. The cation $Ag^.$ thus liberated (from the silver sulfate) is then estimated in the way described above.

Finally it has to be remarked at least briefly that for the determination of some components entirely new methods can be elaborated, by which then with the use of a trickling pipette the accuracy of estimation is very substantially increased. In my preliminary communication (3) I mentioned such a method which I had elaborated already earlier for the determination of minute quantities of *c o p p e r,* as this metal comes very often into consideration in museums. First it is necessary to separate after the known methods the copper from the other metals accompanying it with an able specific treatment. For this the precipitation of copper with benzoinoxime (cupron) or cupferron can be used. The precipitate obtained is, after filtration or centrifugation, suitable washing and burning, transferred into cupric oxide easily soluble in nitric acid. The cupric nitrate formed by the vaporisation of the solution to dryness is liberated from excess of acid. It is only in this solution, which does not contain any other metal than copper, that the precipitation of copper as cupric iodate, $Cu(IO_3)_2$ can be carried through. Though this salt is considerably soluble in water, this solubility can be lowered to a quite insignificant amount by adding ethanol. The precipitation of cupric iodate has to be carried out by means of a neutral solution of lithium iodate (with 25 per cent I_2O_5), as by the action of HIO_3, because of its considerable acidity, precipitation would not be quite perfect. To the solution of cupric nitrate in the centrifuge cone a solution of $LiIO_3$ is added, and heated by placing in hot water. Then it is taken out and absolute ethanol is added in a volume amount larger by about one half than the volume of the solution. After stirring with

a glass rod and after one hour's standing the precipitated $Cu(IO_3)_2$ is centrifuged. For washing it 96 per cent ethanol has to be used. $LiIO_3$ can well be used for the precipitation in an excess of about ten times against the amount theoretically needed for the precipitation of the copper. The excess of $LiIO_3$ is easily removed from the precipitate, as $LiIO_3$ is not only very soluble in water but also in aqueous solutions of ethanol.

The following equation applies for the direct iodimetric estimation:

$$Cu(IO_3)_2 + 12 \, HI = CuI + 13 \, I + 6 \, H_2O.$$

Thus one atom Cu corresponds to thirteen atoms I, so that in using a Bang microburette 0.01 ml. 0.01 N $Na_2S_2O_3$ would indicate only 0.49 micrograms Cu; thus already by this method alone the accuracy of determination is considerably heightened. A much greater accuracy is of course reached when instead of direct titration with thiosulfate we use the trickling pipette with a solution e. g. of 0.01 N $Na_2S_2O_3$ containing simultaneously also a great amount of a calcium salt, e. g. nitrate of calcium.

As, however, cupric iodate is obtained as a precipitate, therefore in a centrifuge cone, a pipe tube cannot be used for the further treatment. To the washed precipitate of $Cu(IO_3)_2$ we add into the centrifuge cone some 4 N $HClO_4$ (not stronger!), then a crystal of KI, and from the trickling pipette a solution of $Na_2S_2O_3$ (e. g. 0.05 normal) is left to trickle out, with a great content of calcium nitrate; finally a little starch solution is still added. (Sulfuric acid cannot be used for acidification as little soluble calcium sulfate would be precipitated, which previous to the precipitation of calcium oxalate would have to be dissolved in too great a volume of distilled water. Perchloric acid is very stable and the ion IO_3' cannot act on it as oxidising agent, in contradistinction to hydrochlorid acid. After very strong acidification the ion I' on the other hand would be oxidised already by atmospheric oxygen.) The liquid is stirred with a glass rod drawn out to a fine (0.05 mm) point.

After reaching the equivalence-point the amount of calcium, which earlier entered the liquid, is determined by titrating its oxalate. Though the whole procedure of copper determination is taking rather a long time, amounts of 1—5 micrograms Cu can thus be determined with exceptional accuracy. In order that it may not be necessary still to carry out the whole procedure for accurate comparison with a known amount of copper, it is preferable to fill the trickling pipette with a solution, prepared before the determination, by mixing a certain volume of the solution of calcium salt accurately with an equal volume e. g. of 0.01 N $Na_2S_2O_3$. The best way to prepare such a solution will be discussed in the final section giving supplements to the general manipulative technique.

In the cases given I used a solution of calcium nitrate which contained in 1.00 ml. 12.2 mg. Ca¨. For filling the trickling pipette a mixture of this solution with an accurately equal volume of 0.1 N $Na_2S_2O_3$ was used. The solution thus obtained was then sucked into the pipette through its fine tip. To the amount of 12.2 mg. Ca¨ there thus corres-

ponded 1.00 ml. 0.1 N $Na_2S_2O_3$ or 0.49 mg. Cu (after the equivalency derived and given already earlier), so that 0.1 mg. Ca¨ determined permanganometrically indicates an amount of 4 micrograms Cu. By using a Bang microburette, i. e. with the possibility of reading off the volume of the solution with an accuracy of 0.01 ml., it was thus possible to estimate by means of 0.01 N $KMnO_4$ (for titration of calcium oxalate) the content of copper with an accuracy of 0.05 micrograms of copper. This example has been given on purpose in detail so as to show concretely how the sensitivity and accuracy of a determination can be increased very greatly also without the use of a special and expensive microchemical apparatus, by the mere introduction of new methods and new working principles.

IV. Examples of the Practical Determination of Some Constituents.

In valuating museum material especially in archeology and numismatics it is often important to determine in the given objects the content of copper. As, however, from the objects (e. g. coins) one can often take without visibly damaging them only minimum quantities of the sample needed for analysis it is necessary to elaborate very fine methods of chemical investigation for valuating such objects. If a microchemical balance is not at one's disposal, it is necessary to restrict oneself only to tracing the mutual ratio of the different constituents, in metal alloys e. g. the ratio of copper to silver, and to estimate these constituents as accurately as possible in a suitable way. For this purpose I tried to elaborate the prescriptions and procedures given below.

Besides the procedure for the determination of minute quantities of *copper,* as described above, one can determine copper by means of the trickling pipette and also in other ways. Thus e. g. one can, after adding a crystal of KI, introduce a weak solution of $Na_2S_2O_3$ with a very strong admixture of a calcium salt from the trickling pipette directly into the liquid in the pipe reaction tube, and after reaching the equivalence-point (finally after the addition of the starch solution) estimate the amount of calcium introduced into the examined liquid. It is, however, a drawback that the solution of starch can be partly mechanically drawn into the precipitate of calcium oxalate, and thus the consumption of permanganate in the titration is increased. To prevent this the thickened solution has to be warmed some minutes with an equal volume of concentrated nitric acid, by which the starch is disintegrated (transferred in oxalic acid). For the rest it is enough for the given purpose when the liquid loses its colloidal turbidity and becomes clear.

Another metal very often coming into consideration in historic objects in museums is *silver.* Though by means of the trickling pipette its determination can be carried out in several ways, we shall mention only the one in which one starts from the pure solution of silver salt alone. For the rest it is of course necessary to separate the silver previously from the other metals in the form of chloride, to reduce the latter (e. g. in an ammoniacal solution by glucose), and after the separation of metallic silver and after washing it (using an electrically driven

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IV. Examples of the Practical Determination of Some Constituents.

In valuating museum material especially in archeology and numismatics it is often important to determine in the given objects the content of copper. As, however, from the objects (e. g. coins) one can often take without visibly damaging them only minimum quantities of the sample needed for analysis it is necessary to elaborate very fine methods of chemical investigation for valuating such objects. If a microchemical balance is not at one's disposal, it is necessary to restrict oneself only to tracing the mutual ratio of the different constituents, in metal alloys e. g. the ratio of copper to silver, and to estimate these constituents as accurately as possible in a suitable way. For this purpose I tried to elaborate the prescriptions and procedures given below.

Besides the procedure for the determination of minute quantities of *copper,* as described above, one can determine copper by means of the trickling pipette and also in other ways. Thus e. g. one can, after adding a crystal of KI, introduce a weak solution of $Na_2S_2O_3$ with a very strong admixture of a calcium salt from the trickling pipette directly into the liquid in the pipe reaction tube, and after reaching the equivalence-point (finally after the addition of the starch solution) estimate the amount of calcium introduced into the examined liquid. It is, however, a drawback that the solution of starch can be partly mechanically drawn into the precipitate of calcium oxalate, and thus the consumption of permanganate in the titration is increased. To prevent this the thickened solution has to be warmed some minutes with an equal volume of concentrated nitric acid, by which the starch is disintegrated (transferred in oxalic acid). For the rest it is enough for the given purpose when the liquid loses its colloidal turbidity and becomes clear.

Another metal very often coming into consideration in historic objects in museums is *silver.* Though by means of the trickling pipette its determination can be carried out in several ways, we shall mention only the one in which one starts from the pure solution of silver salt alone. For the rest it is of course necessary to separate the silver previously from the other metals in the form of chloride, to reduce the latter (e. g. in an ammoniacal solution by glucose), and after the separation of metallic silver and after washing it (using an electrically driven

centrifuge) to transfer it with nitric acid in a solution of silver nitrate, which then is submitted to treatment.

For the precipitation of silver salt solution with thiocyanate it is best to use an admixture of strong calcium nitrate solution. For this purpose 5.00 ml. solution of 0.1 N NH_4CNS are mixed with 5.00. solution of $Ca(NO_3)_2$, which corresponds to an amount of 0.610 g. $Ca^{..}$. The first phase of procedure corresponds in the main to Volhard's method for the volumetric determination of silver. But instead of ferric alum only a little ferric nitrate has to be added to the solution in the pipe tube, as by the action of the alum the admixed $Ca^{..}$ would be precipitated as $CaSO_4$. The solution has to be weakly acidified by a small droplet of nitric acid. The solution is put into the shorter arm of the pipe tube with a thin-walled capillary pipette as already described above (p. 11). The necessary reagents are introduced into the inside of the shorter arm of the reaction tube with a glass rod drawn out into a very fine point. As the volume of the examined solution is only very small, we have to take care that the operation is terminated as soon as the first reddish shade is reached, which remains permanently. After draining the content of the reaction tube and rinsing it with distilled water into a centrifuge cone calcium is precipitated as oxalate and determined by titrating with the standard permanganate solution.

For a given content of calcium salt in a solution of thiocyanate 610 mg. $Ca^{..}$ correspond to 5.00 ml. 0.1 N CNS', which indicates 53.94 mg. Ag. As in Bang's microburette 0.01 ml. 0.01 N $KMnO_4$ indicate an amount of 10 micrograms Ca, one division of the graduation indicates for the given reagent solution simultaneously 0.8842 micrograms Ag. One can thus determine the amount of 1 microgram Ag with an accuracy of only about 50 per cent, the amount of 10 micrograms Ag with an accuracy of 5 per cent. It is self-understood that the accessory solution of calcium nitrate can be used in a still far greater concentration, and thus also the accuracy of determination can be considerably raised. It is of course necessary to say immediately that very concentrated solutions have already a great viscosity, and that therefore it is necessary for measuring them either to use only washing pipettes, as will be mentioned in the last chapter, or a comparative determination has to be carried out with the prepared mixture by using an accurately known amount of silver.

By the new working method the sensitivity also for the determination of very small amounts of *chlorides* can be substantially increased. In principle one can use the mercurimetric method according to E. Votoček (9), in which, however, a great excess of ferric nitrate is added to the mercuric nitrate solution. For filling the trickling pipette a mixture of 0.1 N $Hg(NO_3)_2$ and of a conrentrated solution of $Fe(NO_3)_3$ in the ratio of 1:1 was used. This solution has a strong rusty yellow colour. Thus a very great accuracy was reached for amounts of 1—10 micrograms Cl'.

In addition to the examined solution we introduce into the short arm of a pipe tube a small droplet of nitric acid and some pulverised sodium nitroprusside. As soon as a persistent weak turbidity is reached

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the content of the reaction tube is washed out into a centrifuge cone, and then we proceed as described above on p. 21. The results for very small amounts of chlorides are rather somewhat higher than corresponds to the theory. If after adding NH_4CNS we let it stand for some time or heat it, a blackish brown precipitate is formed by the action of ammonia. By adding a drop of hydrogen peroxide and heating (by placing the centrifuge cone in hot water) it can, however, be transferred relatively easily into the red brown precipitate of $Fe(OH)_3$. This is then washed, by using centrifugation, by hot water alone. From the amount of iodimetrically ascertained iron the amount of chlorides present in the analysed sample can be determined with great accuracy. By the addition of thiocyanate the mercury present is transferred in a soluble complex compound, in which it persists also after adding ammonia, by which $Fe^{...}$ is, however, precipitated as ferric hydroxide. The presence of a great excess of $Fe^{...}$ does not disturb at all in the determination of chlorides according to Votoček's method.

The determination of small amounts of *b a s e s* has already been mentioned on p. 20. The admixture of KIO_3 in an even if only weakly acid medium cannot unfortunately achieve great concentrations because of the only small solubility of acid potassium iodate in water. When we want KIO_3 to be in excess, then for the given purpose we do not achieve practically a higher acidity than about 0.05 N $H^.$, as with a higher content of HIO_3 acid salt is already precipitated, and the amount of $H^.$ approaches the amount of IO'_3, which is quite unsuitable for the given purpose.

A solution obtained by dissolving 0.7 g. KIO_3 pro analysi (Schering-Kahlbaum) and 0.035 g. I_2O_5 (acidum iodicum anhydr. p. a. Schering-Kahlbaum) in a small amount of water and diluted to a volume of 20 ml. was used for these experiments. This solution represents an acidity of approximately 0.01 N $H^.$. In reality its acidity was, however, slightly less. As the sensitivity of the neutralisation reactions in the presence of common colour indicators is much smaller than in oxidation-reduction reactions, it was necessary to pay attention to the most accurate achieving of the right colour change in the equivalence-point, and also the volume of the solution had to be carefully considered. The acid mixture was added from the trickling pipette to the investigated sample of the base only until the first, just certainly discernible change from yellow to orange. It was compared with equal volumes of acid, neutral, and alkaline solutions in tubings, closed by melting, just as wide (2 mm. of inside diameter) as the reaction tube and with an equal amount of methyl orange.

After neutralisation of 0.01 ml. 0.01 N NaOH with iodate mixture from the trickling pipette the volume of the examined solution increased to about 0.02 ml. At the iodimetric titration of this liquid by means of Bang's microburette 0.93 ml. of 0.01 N $Na_2S_2O_3$ was required. With a comparative determination with the amount of 0.02 ml. distilled water alone it was found that for reaching the same colour tint 0.44 ml. of 0.01 N $Na_2S_2O_3$ was required. Thus in the first case after the treatment of 0.01 ml. 0.01 N NaOH only 0.49 ml. of 0.01 N $Na_2S_2O_3$ was finally

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really required. By using a small reaction tube (2 mm. inner diameter) one can determine with this accuracy in a volume of 0.01—0.02 ml. only an amount of up to 2 micrograms OH'. For larger amounts it is better either to use larger reaction tubes or to use instead of KIO_3 another auxiliary substance, e. g. $Ca(NO_3)_2$, which has not yet been examined. In this latter case the determination would of course take a much longer time.

The given method has much greater possibilities in the estimation of acids, as in a weakly alkaline reagent solution even a very great amount of iodate remains, and thus also a very favourable relation of OH' to IO_3' is achieved. By the use of very soluble iodates (e. g. $LiIO_3$) as admixtures it is possible to increase the sensitivity of the method especially much. Generally speaking it may be said that the advantage of using iodates as inert admixture is that in the end they can be very easily and very accurately estimated iodimetrically, and that the ion IO_3' is rather unusual so that it is not likely to be present in the examined sample already beforehand. It is, however, a drawback that the ion IO_3' in an acid medium easily reacts with reducing agents.

If for the analysis an insoluble substance is to be used, prepared by an appropriate preliminary treatment (by centrifugation of a precipitate), then instead of a pipe-tube a centrifuge cone has to be used. Such a case may arise e. g. with the determination of small amounts of calcium. The trickling pipette is filled with a solution of sodium chloride with a small amount of potassium permanganate (e. g. 9 volumes of saturated NaCl-solution and 1 volume of 0.1 N $KMnO_4$). The details of the manipulation technique, which is a little different from those described so far, will be given in the final section. After reaching a persistent pink coloration the chlorides in the liquid obtained are estimated mercurimetrically according to V o t o č e k's method (9). For the given reagent mixture (solution of $KMnO_4$ + NaCl) it is necessary to determine the amount of calcium which corresponds to a volume of 0.01 ml. of the $Hg(NO_3)_2$ solution. This can be done experimentally or by calculation, provided of course that in this latter case the concentrations of the substances in the solutions used are accurately known, and provided that the solution of NaCl was mixed in a definite, accurately known ratio with the solution of $KMnO_4$. This operation is best carried out shortly before the determination. For the acidification of the calcium oxalate suspension perchloric acid or nitric acid (not sulfuric acid an of course in no circumstance hydrochloric acid) has to be used. The simultaneous excess of chlorides has no influence whatsoever on the amount of permanganate used. The manganous salt formed in a small amount does not disturb at all in the final mercurimetric determination.

The few examples given above for the estimation of minute quantities of certain components will perhaps make the possibilities of the new working method sufficiently clear and give the necessary information concerning the concrete problems which arise in its application.

V. Supplements to the General Manipulation Technique

In order to prevent confusion arising out of an excessive accumulation of data on some points treated of in the preceding sections, certain supplements, mainly of a purely practical character, were deferred for treatment till this final section. In supplementation to the determination of calcium (p. 26) it has to be remarked that the centrifuge cone with washed calcium oxalate has, when the permanganate solution is added, to be immersed in hot water in a beaker. The stirring of the suspension is best done by a glass rod drawn out in a fine point and not for instance by a gas stream from a capillary tube. Centrifugation was carried out in cones of 7—10 cm. length, obtained by drawing out Jena test tubes "Fiolax" (of an inner diameter of 10 mm. and a length of 120 mm). Perchloric acid is in the given case suitable for the acidification of the suspension of calcium oxalate as it is very strong, very stable with regard to the oxidation-reduction processes (at least in dilute aqueous solutions), and especially as its calcium salt is very soluble in an aqueous solution.

In order to obtain accurate results it is specially important to observe the correct way of *washing the precipitates* and of available cleaning the upper (wide) part of the centrifuge cones. I have already dealt earlier (6) with this second problem. After the first centrifugation of the precipitate it is always necessary to wipe the whole interior of the wide upper part of the centrifuge cone thoroughly with
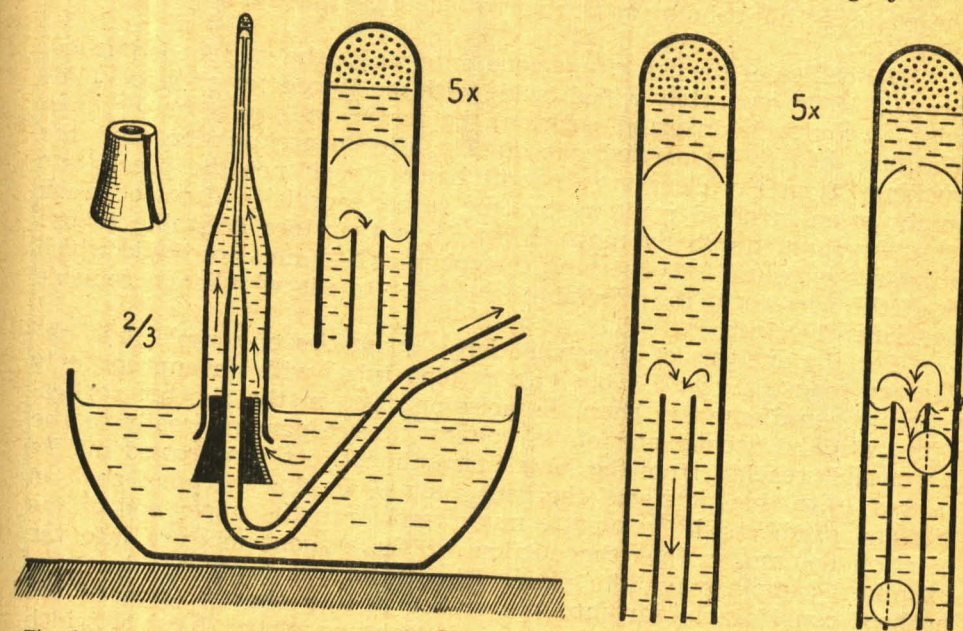

Fig. 4. Arrangement for washing the wide part of the centrifuge cone. Tip of the centrifuge cone in lowering the suction tube and with the emergence of the orifice of the cone from the water.

a small glass rod with a short piece of rubber tubing fitted over its end ("policeman"), so that the precipitate thus loosened from the walls is scattered in the clear liquid. After rinsing the end of the glass rod with water we centrifuge again. It is not until this second centrifugation has been done that the clear supernatant liquid is sucked off by means of a pipette drawn out into a fine and long tip and connected to a suction pump, until the liquid stands, about 1—2 mm. from the precipitate settled in the fine end of the centrifuge cone. Then the centrifuge cone is turned upside down with the orifice downwards and closed with a rubber stopper through which passes a fine straight tubing reaching to the pointed end of the cone, but still a little from the precipitate. The outer part of the glass tubing projecting from the stopper is strongly bent in the shape of the letter V. The rubber stopper has on the side a groove-like incision in the direction of its axis. After closing in with the stopper the lower part of the centrifuge cone is immersed in a deep dish with distilled water and the tube is connected with a filter pump. (Fig. 4.) In the suction of the air the water penetrates through the groove in the stopper into the cone turned with the orifice downwards, and streams to the narrow upper end of the cone where it tumbles down into the tip of the suction tube and is sucked out. Thus the whole centrifuge cone is thoroughly washed and freed completely from all disturbing substances which are adsorbed on the glass surface (excess of reagent solutions). By an appropriate shifting of the tube through of the stopper or emersion of the stopper from the water the height of the water or air column in the narrowed upper part can be regulated (Fig. 4).

The orifice of the centrifuge cone, into which the stopper is pushed, has still to be separately wiped inside with moistened cotton wool (likewise of course in inverted position), before as well as after washing. Washing has to be carried out quickly after centrifugation and the sucking off of the clear supernatant liquid, for if not the precipitate might in an inverted position in some cases, especially after too weak centrifugation, gradually move down. It is therefore desirable to use a magnifying glass for observing the column (1—2 mm.) of liquid which is at the surface of the precipitate in order to see whether it remains permanently clear.

For the analysis of somewhat large quantities of sample it is necessary to use a *reaction tube* (pipe tube) with an appropriately larger inner diameter. Then the solution rises in the shorter vertical arm until the second end of its column (corresponding really to the lower end) reaches from the longer arm almost to the narrowed middle part, i. e. to the middle of the bent tubing. In this marginal position the end of the trickling pipette must reach into the upper end of the solution column so that the outflow of the reagent mixture into the examined sample may take place. The tip of the trickling pipette is pushed considerably far into the orifice of the shorter arm of the reaction tube and carries at least one, better two rubber discs, by which the end of the trickling pipette is centered so that it cannot touch the moist inner wall of the reaction tube, as this would lead at once to
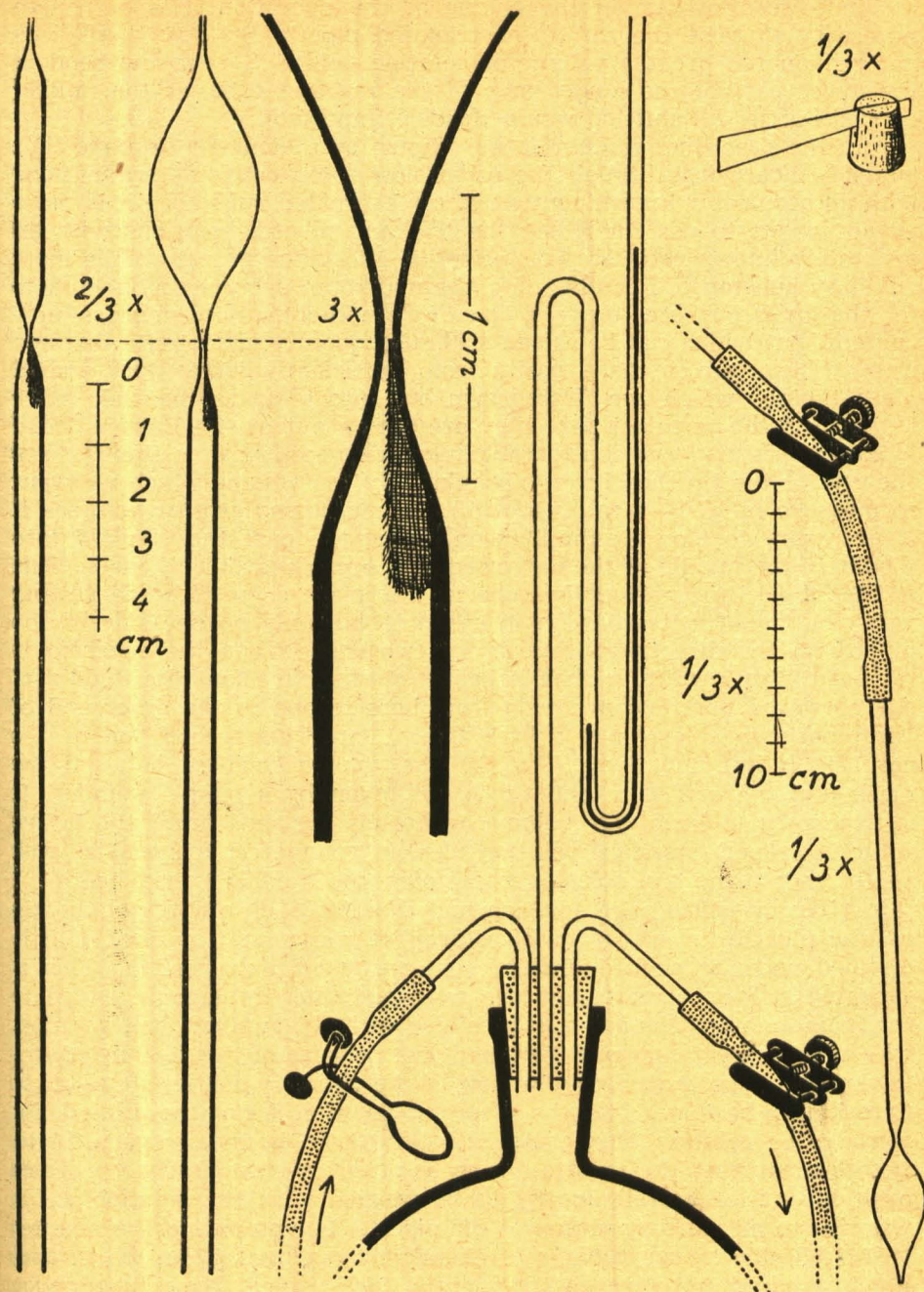
Fig. 5. Washing pipettes, upper part of the bottle with compressed air, drying of washing pipette with filtered air and cork with a paper ribbon.

an undesired outflow. In the course of the operation it is of course necessary to raise the tip of the trickling pipette, so that there does not remain too great a volume of solution behind the narrow bend in the lower part of the longer arm of the reaction tube, as the mixing carried out by its shifting would then be imperfect.

In the preceding chapter it was shown by a concrete example that instead of carrying through the often slow comparative determinations with an accurately known content of the estimated substance it is more advantageous to use for filling the trickling pipette solutions with an accurately known ratio of their effective substance proper to the inert auxiliary substance. For obtaining the maximum accuracy it is suitable for the given purpose to use *pipettes* without a determined simple content, but which can be rinsed still subsequently inside with distilled water. They can be made easily from sufficiently wide, thick-walled glass tubings which are first drawn out into a tip at the end. After cutting off the terminal part they are drawn out at the Bunsen flame in some place also to a considerable narrowing so that from this place to the end of the tip they have approximately the volume which we want to measure (e. g. 1—2 ml.). (Fig. 5.) For measuring greater volumes it is necessary to blow at the Bunsen flame the part thus limited into a bulb. In the middle of the narrowed part a mark is sharply made. This is best done by covering the tube in this place e. g. with red sealing wax (for instance its solution in ethanol), but only on one side of the pipette in the directions towards its two ends. Then the covering is removed with a knife so that it begins sharply in about the middle of the narrowed part and proceeds from here to one or the other end of the pipette in a length of a little over 1 cm. This second end of the covering is left undefined. (Fig. 5.) The volume enclosed between the mark and the orifice of the tip is not given by a simple number. It is necessary to keep this volume accurately for measuring the active solution proper (standard solution used in volumetric analysis) as well as for measuring the solution containing the auxiliary inert salt.

After measuring the solution and draining it into a vessel the tip of the pipette is washed with a drop of water and at once a little distilled water is sucked inside, just sufficient for rinsing. This is repeated still once more, and the washings thus formed are added to the main amount. The same is done also with the auxiliary salt solution, which has a great concentration, and just because of this it is necessary to rinse the pipette perfectly in view of the viscosity of the salt solution. Care has to be taken that the resultant solution is not too diluted, for already the solution of the effective substance is usually very dilute. Before measuring the pipette has to be of course completely dry inside or it has at least preliminarily to be washed with the solution which we wish to measure by means of the pipette. For preparing the pipettes it is advisable to use tubings of chemically resistant glass, which does not fuse easily and which is sufficiently thick-walled. The concentration of the resulting mixture is of no importance, but the ratio of its two components is. In contradistinction to the solutions used in volumetric analysis the loss of water caused by evaporation thus does not cause any error in the result of the analysis.

Considerably thickened *solutions of accessory auxiliary substances* [e. g. a neutral solution of $Ca(NO_3)_2$ or $Fe(NO_3)_3$] for filling the trickling pipette are better prepared in fairly large amounts and stored so that their content remains stable and there is no need to control it. For this purpose we can use e. g. a 100 ml. reagent bottle, in which the glass stopper is replaced by a rubber stopper previously impregnated in fused vaseline during simultaneous evacuation. When there is no guarantee that the bottle glass is sufficiently resistant, the bottle has previously to be covered inside with paraffin. In order that the paraffin layer should not peel off from the wall of the bottle in the course of time, it is well to etch the bottle inside with gaseous hydrogen fluoride, thoroughly rinse with water with simultaneous mechanical wiping of the inside, and then dry. The concentration of the component which comes into consideration (Ca, Fe, etc.) must be accurately estimated by a suitable analytical method and should be marked for a volume of 1 ml. directly on the label of the storage vessel. When we use inner rinsing pipettes like those just described above, then it is necessary to determine the volume they indicate, either from the weight of the mercury they enclose or through neutralisation from the amount of decinormal base or acid of the same volume. For the rest it would of course also be sufficient to determine how much the volume of storage solution—accurately determined by means of a pipette—contains of the component under consideration. When necessary it is better to purify the solutions by means of centrifugation than by filtration, as the very narrow outflow orifice of the trickling pipette might otherwise become stopped already by a relatively small impurity.

In the repeated putting away of the volumetric pipette for inside rinsing it has to be *dried inside by a stream of air*. For this a large empty bottle (of at least 5 litres) closed with a rubber stopper is suitable. (Fig. 5.) Through one tubing air is pumped into the bottle with a rubber bulb and immediately after the pumping the tubing is closed either by a pinchcock or by a glass stopcock. To the other tubing bent downwards, through which the air leaves the bottle, the pipette to be dried is attached with a rubber tubing so that it hangs down. Through a third hole in the rubber stopper an improvised mercury manometer passes, in which the mercury is in the lower portion of the tubing bent in U-shape. The rubber stopper has to be tied to the neck of the bottle so as not to be ejected from it by a greater pressure. The intensity of the streaming of the air is estimated from the deflection of a paper ribbon placed with the surface in front of the tip of the hanging pipette. It is advisable to fix the ribbon of paper with one end into a slot in a cork stopper cut across at the narrower end for this purpose. The drying is accelerated when the interior of the pipette washed with distilled water is still briefly rinsed with aceton or methanol. Before putting it away it is necessary to put on the pointed tip of the washing pipette a small test tube which has in its orifice either a piece of rubber tubing or a rubber stopper with

an appropriately large hole, so that the tip of the pipette is protected from breaking off. All this applies in the main also to the drying and storing of trickling pipettes through which the air streams with still greater difficulty, as they are at their end much narrower than the volumetric pipettes. For their drainage we can use with advantage a double rubber bulb for blowing, to which the trickling pipettes are connected by a rubber tubing, while they are firmly held by a clamp and turned downwards with the fine tip.

For introducing the solution sample into the shorter arm of the bent reaction tube it is better to use *thin-walled hair-tipped pipettes* (p. 11, Fig. 3), as their tips are more elastic than those of thick-walled ones, and thus there is less danger of their breaking off. For comparative estimations with a known amount of the estimated substance by means of very dilute standard solutions it is necessary to graduate accurately the long pipette tip for a certain small volume either with mercury or e. g. by means of neutralisation (p. 31). For this we need instead of a fixed mark a thin rubber disc fixed to the tip of the pipette in the relevant place and to note in the records in millimetres its distance from the outlet of the pipette together with the size of the corresponding volume (e. g. 122 mm., 0.01 ml.). Then only the mark can be firmly traced by means e. g. of sealing wax as described above (p. 30).

The new working technique described in this paper is used also for the determination of still other elements and important constituents whose content is decisive for the correct valuation of natural and historic objects.

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FERDINAND PRANTL a BOHUSLAV RŮŽIČKA

Mnataia nov. gen., nový mlž z českého devonu

Mnataia nov. gen., Новый моллюск чешского девона

Při svém soustavném studiu drobných mlžů ze středočeského devonu nalezli jsme ve vápencích chotečských — $g\gamma_2$ u Holyně další, velmi zajímavou a svéráznou formu, kterou považujeme za novou a kterou proto označujeme jako *Mnataia přibyli nov. gen., nov. spec.*

Vymezení této nové formy sice zakládáme jen na význačných znacích jediné nám dosud známé, neúplně zachované levé misky, kterou však považujeme za tak charakteristickou, že postačuje k jejímu druhovému i rodovému odlišení. Bližší taxionomické zařazení této formy ponecháváme až na další otevřené, i když na druhé straně jsme přesvědčeni o tom, že *Mnataia přibyli nov. gen., nov. spec.* náleží s největší pravděpodobností do skupiny mlžů pseudocyrtodontního typu. Za nejvýznačnější rozlišující rodové znaky této nové formy považujeme charakteristický tvar zámku, typ ozubení i celkový tvar misky.

Z ostatních dříve popsaných pseudocyrtodontních mlžů upomíná *Mnataia nov. gen.* nejspíše na rod *Šufia* Prantl a Růžička, 1955 a do jisté míry i na rod *Parallelodon* Meek & Worthen, 1886. Z ostatní nám přístupné literatury o devonských mlžích neznáme žádnou jinou formu, která by na níže popisovaný rod *Mnataia nov. gen.* upomínala a kterou by bylo možno s ním blíže srovnávat.

*

Результатом нашего систематического исследования в области мелких молюсков чешского девона является следующая очень интересная и своеобразная форма, которую мы обнаружили в хотечских известняках — $g\gamma_2$ (средний девон) у Голыне, и которую считаем новой и поэтому ее обозначаем *Mnataia přibyli nov. gen., nov. spec.*

Определение этой новой формы мы основываем а то, как упоминаем ниже, только на характерных знаках единственной, неполне сохраненной левой створки, которые однако считаем так характер-

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