	H = 1.	O = 16.
Tellurium	126.52	127.49
Terbium	158.80	160.00
Thallium	202.61	204.15
Thorium	230.87	232.63
Thulium	169.40	170.70
Tin	118.15	119.05
Titanium	47.79	48.15
Tungsten	183.43	184.83
Uranium	237.77	239.59
Vanadium	50.99	51.38
Ytterbium	171.88	173.19
Yttrium	88.35	89.02
Zinc	64.91	65.41
Zirconium	89.72	90.40

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 26.]

THE VOLUMETRIC DETERMINATION OF COBALT.[1]

By HARRY B. HARRIS.

Received January 14, 1898.

INTRODUCTION.

ZINC, manganese, nickel, and cobalt constitute an analytical group of more than ordinary importance. The methods for the quantitative determination of these metals are mainly gravimetric. The volumetric methods applied in the estimation of zinc have won a permanent place with the analyst, and are used daily, where zinc determinations are of prime interest.

The estimation of manganese by means of potassium permanganate according to the recommendation of Volhard has almost completely supplanted the methods ordinarily used with that metal. When nickel and cobalt are brought to the front, and when the methods proposed at various times for their determination are carefully examined, it will be found that volumetric processes must be relegated to a very subordinate position.

Accurate, rapid, volumetric methods, giving satisfactory results for these two metals, would be welcomed by all analysts. It is true that volumetric methods have from time to time been brought forward, yet they seem not to have met with favor:

[1] From a thesis presented for the degree of Doctor of Philosophy, 1897.

at least they have not gained a permanent hold in the literature pertaining to analysis.

In the hope that perhaps a careful review of some of the proposed schemes for the volumetric determination of cobalt would disclose their inherent weakness with the discovery of modifications which would lead to their elimination and the improvement of the methods, the present investigation was undertaken. The review includes about every method which has been published upon the subject under discussion.

PREPARATION OF MATERIALS.

It seemed advisable not to use the ordinary salts of the market, but to derive the cobalt from some source after careful purification of the same.

To this end, recrystallized, dry, and pure purpureo-cobalt chloride was reduced by means of purified hydrogen in a porcelain crucible. The bright metallic mass after cooling in hydrogen was transferred to a weighing bottle which was preserved in a vacuum desiccator. Portions of this purified metal were weighed off for the several determinations that were made.

REVIEW OF METHODS.

I. WINKLER'S METHOD.

In the *Zeitschrift für analytische Chemie*, 3, 420, Clemens Winkler called attention to the fact that potassium permanganate will oxidize cobaltous salts; although the precipitation of the cobaltic oxide is not in any sense complete unless there be simultaneously present some substance which will mechanically carry down the cobalt oxide formed.

The reaction was conceived to proceed in the sense of the following equation:

$$6\ CoCl_2 + 5\ HgO + K_2Mn_2O_8 + H_2O =$$
$$3\ Co_2(OH)_6 + 5\ HgCl_2 + 2KCl + 2MnO_2H_2O.$$

The purpose of the mercuric oxide is merely to mechanically separate the cobaltic oxide from the solution. The method seemed to be, in the main, very satisfactory.

As indicated in the equation, the salt used was the chloride. The oxidation is retarded by sulphuric acid, while even traces of other oxy-acids prevent it. The presence of organic substances is harmful, but ferric salts are without influence.

So far as can be determined from the various papers by Winkler upon this method, he operated in the cold. No mention is made of this point, although the succeeding work will prove that it is a matter of moment.

Indeed, it was observed when operating in the cold that when the point of complete oxidation was approached the solution frequently acquired a muddy appearance, and that the action of the permanganate was decidedly sluggish, consequently the end of the reaction was noted with difficulty.

In *hot* solutions, on the contrary, the end reaction was comparatively sharp and the pink color observed without great effort. In the trials made, the solution of the chloride was brought to boiling ; the mercuric oxide was then introduced and the permanganate added, with frequent shaking of the containing flask. The precipitated mercuric oxide was found to be the most suitable, it being more efficient in the precipitation of the cobaltic oxide.

The mercuric oxide was preserved, according to the recommendation of Winkler, as an emulsion, and was so added as occasion demanded. Experience demonstrated that when the cobalt content of the solution was high, it was advisable to dilute it with water to one-half or even more. This facilitated and made more certain the reading of the end reaction. The permanganate usually consisted of about four grams of the pure salt dissolved in one liter of water. A solution of cobalt as chloride, containing 0.1334 gram, was first used.

When the analysis was conducted as outlined above, the following results were obtained :

	Gram.	Per cent.
1	0.1332	99.85
2	0.1329	99.62
3	0.1323	99.17
4	0.1332	99.85
5	0.1338	100.30

These determinations were made in boiling solutions, and confirm the statement that in the cold the reaction is so slow that its conclusion cannot be sharply determined.

To verify this, the results which were gotten when operating in the cold are introduced, the solution used containing 0.1334 gram cobalt as the chloride :

	Gram.	Per cent.
1	0.1253	93.93
2	0.1253	93.93
3	0.1244	93.25
4	0.1241	93.03

The cobalt content of the solution was reduced and a series of oxidations carried out in the same manner as before, observing every precaution.

With a cobalt solution of 0.0534 gram operating in *hot solution* the results were :

	Gram.	Per cent.
1	0.0527	98.67
2	0.0529	99.05
3	0.0518	97.00
4	0.0536	100.38
5	0.0533	99.81

while in the cold there was obtained:

	Gram.	Per cent.
1	0.0503	94.11
2	0.0503	94.11
3	0.0501	93.71
4	0.0491	91.83

The cobalt content was now increased to 0.2668 gram with the following result in *hot* solution :

	Gram.	Per cent.
1	0.2649	99.31
2	0.2646	99.21
3	0.2639	98.94

In *cold* solution:

	Gram.	Per cent.
1	0.2375	89.02
2	0.2357	88.36
3	0.2369	88.80

Two facts are obvious in these results, the method is satisfactory and yields concordant percentage when it is carried out in hot solutions. It is also apparent that, as the quantity of cobalt is raised, the results do not approach the theoretical so closely.

As previously observed, the mercuric oxide was found efficacious in withdrawing the cobaltic oxide from solution. Other reagents designed to perform the same function were tried ; thus, in using barium carbonate with a solution of 0.1334 gram cobalt, low end readings were obtained.

	Gram.	Per cent.
1	0.0989	74.14
2	0.0972	72.93
3	0.0936	70.16

Ferric hydroxide was also applied, but it proved worthless.

In the well-known method of Volhard for the determination of manganese by means of potassium permanganate, zinc sulphate is added. With the cobalt salt this was without effect, and evidently for the reason that the action of the permanganate in the case of manganous and cobaltous salts is quite different.

In the first case there is formed an oxide of decidedly acidic character which tends to combine with oxides still present in the solution, and for this the zinc salt is well suited. Whereas in the cobalt salt the oxidation proceeds with the formation of a rather indifferent sesquioxide which must be mechanically carried down.

On using an emulsion of zinc oxide, the oxidation with potassium permanganate proceeded very slowly, the liquid also clarifying with difficulty.

However, on adding to the solution of cobalt chloride, containing zinc oxide, a solution of ferric chloride, the titrations advanced rapidly in hot solutions, and the cobaltic oxide settled out quickly ; this was no doubt due to the influence of the ferric hydroxide. As evidence of the value of the above procedure, the following results are appended :

	Theoretical cobalt. Gram.	Found cobalt. Gram.	Percentage.
1	0.1334	0.1330	99.70
2	0.1334	0.1328	99.55
3	0.1334	0.1332	99.85
4	0.1334	0.1336	100.15
5	0.1334	0.1363	99.50
6	0.1334	0.1363	99.50
7	0.1334	0.1369	99.93
8	0.1334	0.1362	99.42

Cobalt is quite frequently associated in minerals and ores with arsenic as well as with nickel. By the usual method of solution of such compounds, the arsenic, for example, would be brought into the state of arsenic acid, and when in this condition it prevents the oxidation of the cobalt; when nickel is present it was thought that, by means of a double titration in presence of arsenic acid, the cobalt might be determined, but experiment proved the contrary.

Not infrequently copper is found associated with cobalt. How its presence would influence the determination of the latter by the method under discussion seemed of interest, and experiments with this end in view were instituted. The first solution operated upon contained 0.1370 gram of cobalt and 0.0125 gram of copper, and gave upon titration:

	Cobalt. Gram.	Per cent.
1	0.1363	99.49
2	0.1360	99.28
3	0.1359	99.18

When the copper content was raised to 0.0500 gram, the cobalt found was

	Cobalt. Gram.	Per cent.
1	0.1365	99.64
2	0.1362	99.42
3	0.1360	99.28

But on raising the copper to 0.1300 while the solution still contained 0.1370 gram cobalt there was found:

	Gram.	Per cent.
1	0.0804	58.69
2	0.0783	57.15
3	0.0795	58.03

Recalling the fact that when ferric chloride was added to a solution of cobaltous chloride containing zinc oxide, the hitherto murky solution became clear, and allowed of a complete oxidation of the cobalt, the thought suggested itself that possibly the oxidation of cobalt salts in the presence of mercuric oxide would be complete in the cold, if ferric chloride was added, but experiment did not bear out the suggestion. 0.1370 gram of cobalt gave:

	Gram.	Per cent.
1	0.1331	97.16
2	0.1329	97.01
3	0.1335	97.45

Lead is another metal which sometimes occurs associated with cobalt. In solutions of cobalt and lead the cobaltic oxide was almost quantitatively precipitated by potassium permanganate on addition of mercuric oxide and ferric chloride. A solution containing 0.1370 gram cobalt and 0.0120 gram of lead gave:

	Cobalt. Gram.	Per cent.
1	0.1372	100.15
2	0.1369	99.93
3	0.1373	100.22

As the lead content is raised the results depart from the theoretical quite considerably.

In the presence of arsenic acid and ferric chloride the titration of cobalt can be made by means of potassium permanganate, using mercuric oxide to carry down the cobaltic oxide. With these conditions a cobalt solution of 0.1272 gram gave:

	Cobalt. Gram.	Per cent.
1	0.1273	100.08
2	0.1268	99.70
3	0.1270	99.84

With antimony the remarkable observation was made that as the content of this metal was increased the determination of the cobalt became exact. A solution containing 0.1272 gram cobalt and 0.0900 gram of antimony gave on titration:

	Cobalt. Gram.	Per cent.
1	0.1323	104.01
2	0.1317	103.54
3	0.1321	103.85

When the antimony was raised to 0.1700, while the cobalt content remained the same, the solution gave on titration:

	Cobalt. Gram.	Per cent.
1	0.1297	101.97
2	0.1289	101.33
3	0.1304	102.52

But when 0.4400 gram antimony were present with 0.1272 gram of cobalt the results obtained were:

	Cobalt. Gram.	Per cent.
1	0.1274	100.16
2	0.1265	99.45
3	0.1267	99.60

In this review of Winkler's method the conclusions reached are that the results are fairly accurate when the cobalt content is not too great, but that it can scarcely claim recognition as a trustworthy method under most conditions, and that it can in no wise be regarded as equal in value to the ordinary gravimetric methods employed in the estimation of this metal.

Winkler has asserted in the *Zeitschrift für analytische Chemie*, 7, 48, that the method is applicable in the analysis of a speiss holding arsenic and nickel, yet his own results seem to show that the conditions must be accurately known, otherwise the method is faulty.

Work done with these conditions shows that the determinations were least unsatisfactory when the cobalt stood to the nickel in the ratio of 1 : 2; but even then the results were always high.

II. McCULLOCH'S METHOD.

This method appeared in the *Chemical News*, Vol. 59, and, for its execution, requires the following salts for its execution: Potassium bichromate, ferrous ammonium sulphate, and a solution of potassium cyanide. In carrying out the method, the solutions of bichromate and potassium cyanide are brought together in a flask, the mouth of which is closed with a doubly perforated cork fitted with a thistle tube and an exit tube. A few drops of ammonia are added to the solution to neutralize any free acid which may be present, after which the liquid is boiled to expel the air from the flask.

There is next added the solution under examination, which must be hot, then the reaction occurs almost instantaneously and is complete. The cork carrying the thistle tube is no longer necessary.

An excess of a warm concentrated solution of ammonium chloride is now added and the whole boiled for a short time to drive off the excess of potassium cyanide. Nickel sulphate is now added and the cobaltic cyanide is precipitated.

The nickel sulphate also serves to decompose the potassium nickel cyanide which otherwise would combine with the ferrous ammonium sulphate subsequently introduced, with the consequent production of low results. The solution so precipitated is brought together with a known quantity of ferrous ammonium sulphate and after the addition of a few drops of hydrochloric acid it is titrated with potassium bichromate of known strength.

A solution of 0.1144 gram of cobalt when titrated as above, gave with these conditions (25 cc. potassium cyanide and 25 cc. potassium bichromate):

	Cobalt. Gram.	Per cent.
1	0.1032	90.21
2	0.1039	90.82
3	0.1014	88.64
4	0.1000	87.41
5	0.1023	89.42

When the quantity of potassium cyanide was reduced one half, the results obtained were:

	Cobalt. Gram.	Per cent.
1	0.1056	92.32
2	0.1030	90.04
3	0.1000	87.41
4	0.1060	92.67
5	0.1022	89.32
6	0.1004	87.85
7	0.1009	88.20
8	0.1022	89.32
9	0.1015	88.72
10	0.1020	89.15
11	0.0995	86.97

From this series of results, obtained with the exercise of great care, it is obvious that the suggestion of McCulloch possesses little merit in the desired direction.

The wide divergence of these results from the theoretical and from each other, show that the method has defects.

III. FLEISCHER'S METHOD.

In the *Journal für praktische Chemie*, **110**, 49, there is published by E. Fleischer a method intended for the separation of cobalt from nickel, and the subsequent volumetric determination of the separated cobaltic oxide.

The cobalt salt under examination is mixed with an excess of sodium hydroxide and then treated with a solution of sodium hypochlorite.

Both of these reagents are added in excess, as the complete oxidation of the two metals is of primary importance. The solution is brought to a boil and the black precipitate, consisting of the two sesquioxides, after settling, is filtered off and is then treated with a solution of ammonia (1 : 3).

On applying heat the nickelic oxide is reduced completely, leaving the cobaltic oxide unchanged; this is filtered off and brought in contact with ferrous ammonium sulphate and sulphuric acid, when the ferrous salt will be oxidized at the expense of the cobaltic oxide.

The unchanged ferrous salt is then determined by titration with potassium permanganate.

On working with a solution containing 0.1240 gram cobalt and 0.1263 gram nickel, the resulting sesquioxides were treated with dilute ammonia and boiled for a short period; it was then filtered and treated with ferrous ammonium sulphate and titrated as recommended, with the result that there was found:

	Cobalt. Gram.	Per cent.
1	0.1730	139.52
2	0.1730	139.52
3	0.1729	139.44
4	0.1730	139.52

With 0.0496 gram cobalt and 0.1263 gram nickel, following the method with care, I found:

	Cobalt. Gram.	Per cent.
1	0.0620	125.00
2	0.0619	124.86
3	0.0627	125.98
4	0.0651	131.25

With 0.1240 gram cobalt and 0.0506 gram nickel, there resulted:

	Cobalt. Gram.	Per cent.
1	0.1407	113.47
2	0.1400	112.90
3	0.1350	108.07
4	0.1384	111.61

But, on making up an ammoniacal solution of ammonia (sp. gr. 0.96), with three parts water, as recommended, and boiling for a longer period, the results were more concordant.

With a solution containing 0.0915 gram cobalt and 0.1263 gram nickel, there was found :

	Cobalt. Gram.	Per cent.
1	0.0935	102.19
2	0.0937	102.51

On lowering the nickel content to 0.0550 gram and submitting the oxides to the action of boiling ammonia for one hour, the results continued high.

	Cobalt. Gram.	Per cent.
1	0.1097	119.89
2	0.1094	119.56

When the period of boiling was extended to two hours, 0.0915 gram cobalt, in the presence of 0.1263 gram nickel, gave :

	Cobalt. Gram.	Per cent.
1	0.0937	102.62
2	0.0930	101.64

But when the nickel content was lowered to 0.0505 gram and the solution was boiled for two hours, the results were high :

	Cobalt. Gram.	Per cent.
1	0.1048	114.53
2	0.1035	113.11

These results show conclusively that the weakness of the method is in the reduction with ammonia. The proportion of the two metals is also shown to have an effect on the determination: the proportion of 2 cobalt to 1 nickel seemed especially unfavorable.

IV. DONATH'S METHOD.

In the *Berichte*, *1879*, p. 1868, appears a method devised by Donath. It is really proposed as a modification of the Fleischer method. The instability of the sodium hypochlorite is a bar to its general acceptance, as is also the reduction by ammonia.

As a modification, Donath suggests the oxidation by iodine in a sodium hydrate solution, whereby the cobalt is completely converted into the sesquioxide state, while the nickel remains as nickelous oxide. The precipitate may then be filtered off and the sesquioxide brought into a distilling apparatus along with hydrochloric acid, when the following reaction takes place :

$$Co_2O_3 + 6\ HCl = CoCl_2 + 3\ H_2O + Cl_2.$$

The liberated chlorine is conducted into a potassium iodide solution and the liberated iodine is titrated by sodium hyposulphite.

From the iodine found the cobalt can be readily calculated.

On oxidizing a solution containing 0.1263 gram nickel and 0.1240 gram cobalt with thrice sublimed iodine, the results were always high, as the following series will show :

	Cobalt present. Gram.	Cobalt found. Gram.	Percentage.
1	0.1240	0.1414	114.03
2	0.1240	0.1426	115.00
3	0.1240	0.1286	103.71
4	0.1240	0.1240	100.00
5	0.1240	0.1438	115.97
6	0.1240	0.1388	111.93
7	0.1240	0.1607	129.60

But on using chemically pure iodine the results were much closer :

	Cobalt. Gram.	Gram.	Per cent.
1	0.1240	0.1261	101.69
2	0.1240	0.1240	100.00
3	0.1240	0.1235	99.60
4	0.1240	0.1296	102.34
5	0.0496	0.0480	96.57
6	0.0496	0.0491	98.99
7	0.0496	0.0478	96.16
8	0.0496	0.0500	100.81

When the nickel content was reduced to 0.0506 gram with 0.1240 gram cobalt, the results were as follows :

	Cobalt. Gram.	Gram.	Per cent.
1	0.1240	0.1243	100.24
2	0.1240	0.1248	100.65
3	0.1240	0.1236	99.76
4	0.1240	0.1251	100.88

From these results it can be seen that the purity of the iodine is of prime importance, otherwise part of the nickel will be oxidized. The method may be considered as fairly accurate.

V. VON REIS' METHOD.

In the *Zeitschrift für angewandte Chemie*, *1890*, appears an article by M. A. von Reis and F. Wiggert on the determination of cobalt in the volumetric way.

The cobalt solution is treated with an emulsion of zinc oxide and brought to boiling, when a known quantity of a standardized solution of potassium permanganate is added.

The oxidized cobalt falls to the bottom and allows of the back-titration of the potassium permanganate by ferrous ammonium sulphate.

	Cobalt present. Gram.	Cobalt found. Gram.	Percentage.
1	0.1334	0.1330	99.70
2	0.1334	0.1325	99.32
3	0.1334	0.1328	99.55
4	0.1334	0.1334	100.00
5	0.1334	0.1340	100.45

To all appearances this is by far the most satisfactory method yet proposed. Its simplicity recommends it.

CONCLUSION.

After careful repetition of these methods, making varying conditions wherever deemed advisable, one is justified in concluding that none of them possess the degree of accuracy required in any trustworthy determination of cobalt. A good volumetric method for this purpose still remains to be devised.

UNIVERSITY OF PENNSYLVANIA.

RECENT WORK IN ENGLAND ON THE PURIFICATION OF SEWAGE.[1]

By LEONARD P. KINNICUTT.

Received January 24, 1898.

THERE are few questions connected with municipal government which cause as much trouble as the disposal of sewage in such a manner as to prevent any cause for complaint, and it is certainly not far from the truth to say that, at the present time, there is no large inland city in the world that has succeeded in satisfactorily disposing of the refuse matter that passes through the sewers.

---

[1] Read at the Washington Meeting, December 29, 1897.