ON THE SPECTROCHEMICAL DETERMINATION OF VANADIUM IN IRON ORES AND SLAGS

BY

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WITH 7 FIGURES IN THE TEXT

Introduction.

It is a wellknown thing in spectrography, that if one is making quantitative determinations of some chemical element in one sort of material, and then turns to determine this element after the same method in another material, having a base substance essentially different from the first, a trial of the validity of the calibration curve for the new material (the new base) is necessary, often with the result that a new calibration curve must be constructed. In the most favourable case the calibration curves constructed for different bases, are identical or nearly identical, but as a rule one must be prepared to find the curve displaced, because the intensities of the spectral lines applied, may be influenced by the physical conditions prevailing in the arc, and by the manner in which the elements evaporate from different base substances, and these conditions may vary when the dominating substance is e.g. lime, silicates, or metals.

This displacement of the calibration curve may in some cases be of a considerable magnitude, and may necessitate a careful and critical treatment of the analysis results. So L. W. Strock (1) found that the sensitivity of Li is five times higher in a 1:1 mixture NaCl:SiO₂ than in pure quartz.

It may often be advantageous to stabilize the arc temperature by adding e.g. NaCl, albite, SiO₂ or other compounds to the samples in such quantities that these dominate the base substance, or it may be possible to find spectral lines or line pairs, the relative intensities of which are only to a small degree modified by changes in electrical discharge conditions.

The author has often had the opportunity of observing certain irregularities which occur by spectral analyses of vanadium in the arc. These irregularities became especially evident during the composing of methods for spectrographical determination of vanadium, titan-
ium, and other elements in iron ores, and of vanadium in slags, and as the deviations were found to be of a considerable magnitude, the present investigation was started in order to make an attempt to find which components of the base substance are responsible for the deviations, how they influence the intensities of the spectral lines used, and if possible, find a method which reduces the deviations to a minimum.

The Determination of V in Iron Ores Using Fe as a Comparison Element.

By the composing of the spectrographic method for the determination of V in iron ores, 5 magnetites served as standards. According to chemical analyses* these magnetites contained:

<table>
<thead>
<tr>
<th></th>
<th>% V</th>
<th>% Ti</th>
<th>% Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite A</td>
<td>1.17</td>
<td>6.90</td>
<td>57.8</td>
</tr>
<tr>
<td>B</td>
<td>0.83</td>
<td>2.70</td>
<td>64.8</td>
</tr>
<tr>
<td>C</td>
<td>0.50</td>
<td>1.80</td>
<td>65.0</td>
</tr>
<tr>
<td>Crude Ores</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.17</td>
<td>3.18</td>
<td>35.45</td>
</tr>
<tr>
<td>E</td>
<td>0.23</td>
<td>3.18</td>
<td>35.45</td>
</tr>
</tbody>
</table>

In addition to these I have also used the iron ores B and C diluted 1:1 with pure Fe₂O₃.

Now a quantitative spectral analysis can be carried out in many ways, but it is best to compare a spectral line of the element to be determined, with a suitable line of an element occurring in known and large (easily determinable) quantities in the material which is examined, or with a line of an element which is added to all the samples in a definite and so large amount, that traces of this element previously present in the substance to be analysed, do not disturb the analysis.

As to the iron ores, it therefore seems natural and convenient to compare the intensity of a V-line with that of a Fe-line; then a chemical determination of Fe is a fairly easy matter, and especially

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* It may be mentioned here that unintelligible difficulties and wasted work at the beginning, turned out to be due to essentially incorrect V- and Fe-figures, which had been reported according to industrial chemical analyses. E.g. the ore D was reported to contain 0.28% V and 35.0% Fe. The correct figures then have been determined by conservator, engineer K. Kristoffersen.
since from a spectrographical point of view, there seems to be few objections to make against a line-pair V—Fe. Both elements vaporise at about the same rate from the arc, they both have so many lines, that it should not be difficult to find a V-line with a neighbouring Fe-line, both lines being free from disturbing coincidences and having comparable intensities at the V- and Fe-concentrations concerned.

Everything taken into consideration, a determination of V with Fe as a comparison element seemed to be promising and convenient, and consequently a method was prepared for this determination. It is necessary here to describe the method shortly, and especially the construction of the calibration curve from the blackening curves of the V- and Fe-lines.

Method: Among the many V- and Fe-lines 2 line pairs were chosen as well suited for the analysis, namely V I 3185.396 — Fe I 3205.400 and V I 3056.334 — Fe I 3055.263. V 3185 coincides with the weak Ca-line 3185, but this does not disturb the analysis except when the Ca-content is high and the V-line at the same time very weak. When the V-content is as high as in the standard magnetites, this coincidence is of little importance, even if the magnetites are diluted 1:10 with CaCO₃.

Other serious coincidences are not present, except Mo 3055.323, when the samples contain Mo.

The spectrograph used was a large quartz spectrograph constructed by R. Mannkopff in Göttingen. It had a dispersion corresponding to 6.5—7.5 Ångstrom pr. mm on the plates in the region used. The powdered sample, mixed with two parts by weight of carbon powder to get a steady and quiet arc, was packed into a bore 4 mm deep and of 1.5 mm diameter in a pure carbon cathode of 3 mm diameter. The anode carbon had a diameter of 4 mm. After the arc was started, it burned for 3 minutes at a current of 6.5 amps. The method for making the spectra was the one described by L. W. Strock (2), by which the spectra are stepped so as to serve as their own density calibration marks. The 2/3 of the arc nearest to the cathode was projected diffusely on the spectrograph slit, and by rotating a step sector just before the slit, a stepped spectrum was produced. The different steps along each spectral line were thus given exposure times which were in the ratio 1:2:4:8:16:32:64. The spectra were photographed on Perutz graphic plates, which were developed in a Metol Hydroquinone developer.
By means of a recording microphotometer several steps of the selected V- and Fe-lines were photometered. The photometer curves thus achieved, can be used for quantitative analysis after several methods, but here was chosen the method of constructing the blackening curves as this method is the most reliable and accurate.

The blackenings of different steps of the V-and Fe-lines respectively, is calculated from the galvanometer deflections from the equation:

\[ S = \log \frac{I_0}{I} \]

where \( I_0 \) is taken as the galvanometer deflection for an unexposed part of the plate, and \( I \) is the deflection produced by the line whose blackening is to be measured.

The blackening curve of a line shows the relation between the density of blackening of this line on the plate, and the intensity of illumination which produced the line.

Fig. 1 shows an example of the blackening curves of the line pair V 3185 and Fe 3205. The curves show the relation between blackening \( S \) and log relative exposure time, (instead of log relative intensity) since a step sector has been employed (3).

When a spectral line increases in intensity, its blackening curve will move to the left, and since the intensity of a line increases with the percentage of the element concerned, the horizontal distance between the blackening curves of the V- and Fe-lines (\( \Delta \log T \)) is dependent of the concentration ratio V:Fe.

This horizontal difference \( \Delta \log T \), which is here measured in mm (10 mm = log rel. exposure time 0.3) is zero when the V- and Fe-lines are of the same intensity, it is positive when the V-line is the stronger, and negative when the V-line is of less intensity than the comparison line of Fe.

The calibration curve is constructed by plotting \( \Delta \log T \) in mm against log concentration ratio V:Fe. On fig. 2 the calibration curves for the line pairs V 3285—Fe 3205 and V 3056—Fe 3055 are shown.

Such curves are usually linear over wide intervals, and the determination of V is carried out thus: The spectra of the samples to be analysed are photographed as described above, the selected lines of V and Fe are photometered and the blackening curves constructed. Then the distance \( \Delta \log T \) between the linear parts of these curves is measured (\( \Delta \log T \) was measured in mm at the blackening
s = 0.7), and the concentration ratio V:Fe can be read from the calibration curve.

It is seen on fig. 2 that the curves ABC must be considered as good calibration curves, they are as straight as can be expected when one remembers that those curves are founded on chemical analyses of the standards, whereby uncertainties from the chemical determination are also brought in.

But the points D and E do not seem to belong to the calibration curves at all, as a determination of V by means of the curves ABC using e. g. the line pair V 3185—Fe 3205 would give a V content more than 100 relative % too high, and this is an irregularity that by far exceeds the usual deviation of ±10%, and brings into the analyses a dangerous element of uncertainty.

This irregularity was one of the causes of this investigation. The problem first arising was this:
Why do the points D and E fall far outside the curve ABC, and how can reliable spectrochemical analyses of V in iron ores be carried out, and spectrochemical analyses of V in general?

Now the ores D and E are of a chemical combination different from A, B, and C, because A, B, and C are iron ore concentrates, while D and E are crude ores containing at least 50\% of silicate rock, and consequently it can at once be seen that to use the calibration curve ABC for these unconcentrated ores is in disagreement with the general rules for quantitative spectrum analyses, because to ensure good results one must take care that the samples to be analysed and the standard mixtures have approximately the same base substance.

Deviations of this sort caused by differences in the base substance are familiar things often met with in spectrochemical work. L. W. Strock (1) has shown the effect which additions of CaCO$_3$, NaCl, and SiO$_2$ to the samples have upon the intensity ratios $\frac{\text{Li}}{\text{Sr}}$, 6707.86 and $\frac{\text{Li}}{\text{Sr}}$, 6103.59 pointing out that an addition of NaCl gives rise to the intensity of the Li-lines applied, while the intensity decreases when CaCO$_3$ is added. And W. Rollwagen (4) has shown how the influence of different base substances upon the intensities of spectral lines can be explained by variations in the physical conditions e.g. temperature of the arc, caused by these bases.*

The deviations mentioned are in many cases small in spite of considerable difference in the composition of the materials analysed, and it is therefore often unnecessary to construct new calibration curves.

The ideal solution of the problem will of course be to find line pairs the intensity ratios of which are not at all influenced by variations in the base substance, i.e. by variations in the conditions prevailing in the arc (5). But such a line pair is not always easily found, and in practice one must usually be content with less ideal line pairs.

Considering the iron ores D and E the deviations are great, and as those deviations are very likely to be traced to the accompanying rock, it would be of interest to investigate the influence of other materials upon the V-determinations. At my disposal were several

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* See also R. Mannkopf Zeits. f. Physik. 86, 183, 1933.
slags with known V- and Fe-content according to chemical analyses, and these slags were used as standards in the same way as the iron ores. The result was deviations from the iron ore calibration curve far exceeding those found for D and E, the analyses of the slags giving V-contents 6½ times too high, when the line pair V\textsubscript{3185}—Fe\textsubscript{3205} was employed, and about 3½ times too high when the line pair V\textsubscript{3056}—Fe\textsubscript{3055} was used.

This shows that the intensity ratios $\frac{V_{3185}}{Fe_{3205}}$ and $\frac{V_{3056}}{Fe_{3055}}$ are very sensitive against variations in the base substance, but the intensity ratio $\frac{V_{3055}}{Fe_{3056}}$ is less influenced than the ratio $\frac{V_{3185}}{Fe_{3205}}$.

As the deviations of D and E from the iron ore calibration curve ABC, are supposed to be due to the silicate rock which those unconcentrated ores contain, a mixture of D with one of the concentrates e. g. A, must also give an intensity ratio $\frac{V}{Fe}$ deviating from the curve ABC. That this is really the fact, table 1 shows quite clearly, the deviations increasing with increasing addition of D to the mixture, the deviation of D forming the limit.

<table>
<thead>
<tr>
<th>Substance examined</th>
<th>$\frac{V_{3185}}{Fe}$</th>
<th>$\frac{V_{3056}}{Fe}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D alone .................</td>
<td>0.80</td>
<td>+ 3.2 + 11.5</td>
</tr>
<tr>
<td>80% D + 20% A ............</td>
<td>1.30</td>
<td>+ 8.8 + 15.9</td>
</tr>
<tr>
<td>60% D + 40% A ............</td>
<td>1.59</td>
<td>+11.2 +17.2</td>
</tr>
</tbody>
</table>

For a closer examination D and E were subjected to a magnetic separation. In the magnetic parts (magnetite) V was determined by means of the calibration curve ABC, while the influence of the unmagnetic parts upon the V-determination were tested by mixing 7 parts by weight of these silicates with 3 parts of the concentrate C, thus producing a mixture corresponding to D.
If the rock content is the cause of increase in the intensity ratio \( \frac{V}{Fe} \) as to D and E, this rock must have a similar influence when added to the concentrate C.

Table 2 confirms this presumption. The change in \( \Delta \log T \) is of about the same magnitude when the silicates are added to C, as when added to the magnetic concentrates of D and E. (That the change in \( \Delta \log T \) is not ca. 8 mm corresponding to the deviation of D and E from the calibration curve ABC, is explained by the fact that the silicate rock itself contains a considerable amount of Fe.)

<table>
<thead>
<tr>
<th>Substance examined</th>
<th>( \Delta \log T ) in mm V 3185—Fe 3205</th>
<th>Rise in ( \Delta \log T ) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic concentrate of D</td>
<td>+ 8.0 + 11.5</td>
<td>3.5</td>
</tr>
<tr>
<td>C</td>
<td>+ 3.3 + 7.9</td>
<td>4.6</td>
</tr>
<tr>
<td>Magnetic concentrate of E</td>
<td>+ 4.0 + 8.7</td>
<td>4.7</td>
</tr>
<tr>
<td>C</td>
<td>+ 3.3 + 7.8</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Thus it is proved that the irregularities which occur in the spectrochemical examination of D and E, are caused by the influence of the silicates contained in those unconcentrated ores. These silicates give to the intensity ratio \( \frac{V}{Fe} \) a rise (increase in \( \Delta \log T \)) which renders the calibration curve ABC inapplicable to unconcentrated ores still containing rock minerals.

As the rock consists of several components it will be of interest to find out if the increase in \( \Delta \log T \) is due to one single component or to a combination of more of them.

A microscopic examination of the unmagnetic parts of D and E, which Professor Dr. V. M. Goldschmidt was so kind to carry out for me, showed that the unmagnetic rock was composed thus:

Chief component: Hornblende (green amphibole); next: a feldspar of the plagioclase group; subordinately: brown biotite.
In addition to this, the sample contained still a little iron ore, probably ilmenite, a little corundum, and a little garnet. The samples derived from D and E were obviously different, but the difference was not so great as to involve any serious difference in chemical composition.

According to chemical analysis the unconcentrated iron ore E contained:

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>35.45 per cent</td>
</tr>
<tr>
<td>V</td>
<td>0.23 » »</td>
</tr>
<tr>
<td>TiO₂</td>
<td>5.30 » »</td>
</tr>
<tr>
<td>SiO₂</td>
<td>23.00 » »</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.89 » »</td>
</tr>
<tr>
<td>MgO</td>
<td>5.65 » »</td>
</tr>
<tr>
<td>CaO</td>
<td>4.26 » »</td>
</tr>
</tbody>
</table>

The cause of the increase in Δ log T must be found in one or more of the chemical components above, given in the table besides Fe and V, or in a combination of several of these components. Of these TiO₂ can at once be excluded, because D and E do not essentially differ from the other ores in Ti-content, and as A contains even 11.5 per cent of TiO₂ without being influenced by this percentage in any way.

The remaining components to be investigated are SiO₂, Al₂O₃, MgO and CaO, and the influence of these components upon the intensity ratio \( \frac{V}{Fe} \) were tested one by one, by mixing the magnetite C with each of these components in several concentrations. SiO₂ showed no effect, MgO showed little influence, while Al₂O₃ influenced the intensity ratio considerably and CaO had the greatest effect. Ca added in the form of CaCO₃ showed the same effect as when added in the form of CaO.

Fig. 3 shows how the horizontal distance (Δ log T) between the blackening curves of V 3185 and Fe 3205 varies with the added amounts of the more or less active components, the ratio percentage of V percentage of Fe being kept constant all the while.

Assuming that each chemical component of the rock acts as if it were alone, one can calculate the total effect of the umagnetic part of E (58 per cent), by adding up the partial effects of SiO₂, MgO, Al₂O₃ and CaO.
The total increase of $\Delta \log T$ (deviation of $\Delta \log T$ from the calibration curve ABC) for the iron ore E would then be: $-0.1 (\text{SiO}_2) + 0.3 (\text{MgO}) + 2.4 (\text{Al}_2\text{O}_3) + 2.3 (\text{CaO}) = 4.9$ mm. But this is less than $\frac{2}{3}$ of the real deviation of 7.6 mm which was found by experiment.

This shows that the change in $\Delta \log T$ can not be explained merely as a sum of the partial effects of the different chemical components, and there is only one solution possible: The deviations are

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Fig. 3. Influence of CaCO$_3$, SiO$_2$, Al$_2$O$_3$, MgO, olivine, albite, and labradorite-content on blackening curve separation V3185—Fe 3205.

$\frac{\% \text{V}}{\% \text{Fe}} = \text{const.} = 0.0077.$
caused by one or more combinations of these chemical components, and as the chief compounds of the rock concerned are hornblende and feldspar, these must give the solution.

Accordingly a hornblende—feldspar mixture that is added to the iron ore concentrates must produce the effect that the intensity of the V-lines used are increased as compared with that of the Fe-lines, and the deviation from the calibration curve ABC thus found must be in agreement not only qualitatively but also quantitatively with the deviation which D and E show.

The adding of a hornblende—feldspar mixture involves however the disadvantage that the hornblende would bring some Fe into the mixture, and to avoid this, a mixture in composition corresponding approximately to the silicates in D and E were made by thoroughly mixing

1 part by weight of olivine
1 » » » albite and
2 parts » » » labradorite.

The Fe-content of this mixture is so small (1.2% Fe) that it does not seriously influence the analysis.

This olivine—albite—labradorite mixture was added to the concentrates A, B, and C in the proportion, 1 part of mixture to 1 part of the concentrate, carbon powder was added as usual, and of the standards thus prepared spectra were taken in the same way as all the previous spectra. The result was the calibration curves II seen on fig. 4 a and b.

The deviations agree with the deviations from the iron ore calibration curves produced by D and E. D containing 58 per cent of rock falls practically on the curves, while E which contains about 70 per cent of rock falls a little to the left, which is to be expected as the curves are constructed for iron ores containing 50 per cent of rock.

But how does each of the components olivine, albite and labradorite influence the intensity ratio $\frac{V}{Fe}$? How much of the change in $\Delta \log T$ is due to the olivine, and how much to the albite and labradorite?

Fig. 3 shows the influence of these components upon the blackening curve separation $\Delta \log T$ of the lines V $3185$ and Fe $3205$,
when each of these components are added to the concentrate C. By summing up the partial effects of olivine, albite, and labradorite, the total change in $\Delta \log T$, related to the above mixture (1 part of olivine, 1 part of albite, 2 parts of labradorite, and 4 parts of C) is calculated to:

$$0.9 \times 12.5\% \text{ of olivine} + 1.8 \times 12.5\% \text{ of albite} + 3.4 \times 25\% \text{ of labrador} = 6.1 \text{ mm},$$
while the change in $\Delta \log T$ as measured in fig. 4 a is found to be 6.2 mm. The agreement is complete.

Interesting in this connection is the fact that albite and labradorite show about the same effect in spite of their different chemical composition (albite containing about 12 per cent Na$_2$O and no CaO, and labradorite containing 14 per cent CaO and about 3 per cent Na$_2$O). In agreement with this the substitution of labradorite for albite in the above mixtures did not change the result.
In order to find out if the change in $\Delta \log T$ which the other line pair $\lambda 3056 - \lambda 3055$ exhibits could be explained in the same way as shown above for the lines $\lambda 3185$ and $\lambda 3205$, the curves in fig. 5 were constructed. These curves show the influence of olivine, albite, and labradorite upon the blackening curve separation $\Delta \log T$ of the line pair $\lambda 3056 - \lambda 3055$. By adding up the partial effects of olivine, albite and labradorite, the change in $\Delta \log T$ is calculated to: $0.1 + 1.1 + 3.0 = 4.2$ mm. The change measured in fig. 4 b is 4.0 mm.

Here may perhaps also be mentioned some interesting features which the influence of NaCl exhibits, as NaCl might be expected to produce a similar effect as albite.

The concentrate C was diluted 1:19 and 1:1 with NaCl. To the 1:1 mixture 2 parts of carbon powder were added as usual, to obtain a steady and quiet arc, while the 1:19 mixture produced a quiet arc without this addition. The spectra of these mixtures when taken in the ordinary way, showed that NaCl had no influence upon the intensity ratio $\frac{\lambda}{\lambda}$ as $\Delta \log T$ was found to be of the same magnitude as for the concentrate alone.

But when spectra were taken in successive fractions of 1 minute each, some characteristic features became visible. The fractionated exposures showed quite clearly:
1. that the V I-lines 3185—83, 3060, and 3056 increase considerably in intensity as compared with the V II-lines 3125, 3118, 3111, and 3102 when NaCl is added. When NaCl at the end of the first minute has disappeared from the arc by fractional evaporation, this effect disappears too.

2. V and Fe do not evaporate simultaneously and at the same rate, when NaCl is added, as V to a great extent evaporates at the same time as Na, while most part of the Fe remains in the carbon until Na has disappeared. The amount of V evaporating at the same time as the greater part of the Fe is estimated to be less than half of the total V-amount.

1 is an example of the influence which the arc temperature produces upon the intensity of the spectral lines, NaCl causing decrease of the arc temperature. *

2 is an evaporation phenomenon, and shows that Fe is not an ideal comparison element in this connection, and should not be used when great amounts of alkalies are present, as V and Fe in this case do not meet the demands of simultaneous evaporation. However, when NaCl is not added, V and Fe vaporize simultaneously from the iron ores, concentrated as well as unconcentrated. And in spite of this, the NaCl-mixtures give a better result (no change in \( \Delta \log T \)) than the iron ores D and E.

As mentioned before, albite and labradorite produce about the same change in \( \Delta \log T \) when added to the iron ore concentrates. But fractionated exposures showed that while in the labradorite mixture V and Fe vaporize simultaneously, the spectra of the albite mixture show the same features as when NaCl is added, but to a less extent. However no difference in the total exposures of the labradorite and the albite mixtures with regard to the V- and Fe-lines employed could be detected.

This must mean that it is of no great importance in this case that V and Fe should vaporize at the same time. The inconstancy of the intensity ratio \( \frac{V}{Fe} \) seems rather to be due to variations in the arc temperature.

The described increase in \( \Delta \log T \), that is in the intensity ratio \( \frac{V}{Fe} \), when several compounds are added to the iron ore concentrates,

* Phenomena like this and others caused by alterations of the physical conditions of the arc are more closely described by W. Rollwagen.(4)
may arise from an increase of the intensity of the V-lines, from a weakening of the Fe-lines, or from a combination of both.

Concerning CaCO₃ this question was given a closer examination. Fig. 6 shows the photographic density of the Fe- and V-lines, when the ratio \( \frac{\text{percentage of V}}{\text{percentage of Fe}} \) is constant, while the samples contain different amounts of CaCO₃. All the samples were photographed on the same plate in order to eliminate any variations due to the developing process.

It is seen that the density of the V-line 3185 is practically constant up to a CaCO₃-content of 50 per cent, while it should normally be supposed to decrease, but the density of the Fe-line 3205 decreases as expected. Thus it is proved that when CaCO₃ is added, the intensity ratio \( \frac{V}{Fe} \) increases according to a rise in the intensity of V.

An examination of other plates showed that this is also valid in the case of D and E and other cases where \( \Delta \log T \) is found to be greater than expected according to the iron ore calibration curve.
The Determination of V in Slags with Fe as a Comparison Element.

It has been mentioned above that the spectrochemical determination of V in slags is subject to the same effect as the determination of V in unconcentrated iron ores, the only difference being that the effect produced in the slags is much greater. But one must also admit, that it is not to be expected that an intensity ratio \( \frac{V}{Fe} \) related to the slags, should be applicable to the iron ore calibration curve. Then according to K. Kristoffersen (6) the slags employed can roughly be considered as a mixture of Ca-ferrite \((2 \text{CaO} \cdot \text{Fe}_2\text{O}_3)\) and Ca-silicate \((2 \text{CaO} \cdot \text{SiO}_2)\) in the proportion about 1:4, and in addition to this a RO-phase containing FeO, MnO, and MgO. Thus the slags show a base substance quite different from that of the iron ores, the ores containing rock minerals being included. And in addition to this there is also another important difference, as in the slags V and a great part of Fe occur as silicates.

In order to construct a calibration curve applicable to slags, a series of standard mixtures was prepared by diluting a synthetic slag, \( S_0 \), having a V-content equivalent to 2% of the Fe-content, successively with a V-free synthetic slag.

The two synthetic slags were prepared by mixing 58.3% CaO, 25.0% SiO\(_2\) and 16.7% Fe\(_2\)O\(_3\) thoroughly in an agate mortar, V being added in preparing one of them. (Vanadium was added as a vanadium oxide compound containing 50.3% V.) These mixtures were pressed to tablets at a pressure of 1000 kg/cm\(^2\), and then sintered for 18 hours at 1100° C in an electric furnace. The dilution yielded the mixtures \( S_1, S_2, \) and \( S_3 \) having the following V-contents in percent of the Fe-content: 1.0, 0.333, and 0.1.

Of these mixtures spectra were made in the way described above, and fig. 4 shows the achieved calibration curves (III). The curves are greatly displaced relatively to the iron ore curves, and it is seen that when the iron ore curves are used for the determination of V in slags, the figures come out 6½ times too high when the line pair V 3185—Fe 3205 is used, and 3½ times too high when using the pair V 3056—Fe 3055.

The actual slags with known V- and Fe-content according to chemical analysis, which are previously mentioned, yielded the points
enclosed in small triangles. It is seen that the points related to the standard mixtures are lying on a straight line, while those due to the actual slags are not.* But it must be taken into consideration that the absolute V-content of the slags is of the magnitude 0.09—0.15 per cent, and when the chemical analysis in spite of this agree as closely as shown, the check must be considered as good as can be expected.

Some of the slags had been treated with chemical agencies e. g. citric acid, and the residues accordingly had a Fe$_2$O$_3$-content of about 50 per cent, and for these residues new calibration curves must be constructed. As standard mixtures were used the synthetic slags S$_0$ and S$_1$ diluted 1 : 1 with Fe$_2$O$_3$, and the standard mixtures thus contained 58 per cent Fe$_2$O$_3$ and 29 per cent CaO, and the V-content was 0.143 and 0.285 in per cent of the Fe-content.

The resulting calibration curves are as expected displaced to the right relatively to the slag curves, as shown in fig. 4, curve IV.

**An Estimation of the $\frac{V}{Fe}$-Method.**

From the foregoing it will be seen that the quantitative spectrochemical determination of V in iron ores and slags is subjected to certain difficulties. Quite a lot of calibration curves must be applied as fig. 4 shows, if one is going to examine slags, concentrated iron ores, ores containing rock minerals and so on. Though all these curves must be used, the V-determinations might, when caution and care are applied, give results probably not deviating more than ± 10 relative per cent from the real V-content. The analysis of concentrated iron ores is simple and convenient. As to the ores containing rock minerals the case is more complicated, as the ores nature and approximate amount of rock minerals should first be determined by magnetic separation or in some other way. Concerning the slags each slag type should have its own calibration curve.

But in spite of the convenience in using Fe as a comparison element, it must be admitted that the irregularities and disadvantages connected with this method are so great, that an easier method is desirable.

* The flat part of the V 2056 curve is due to the fact that the V-line at this concentration nearly disappears in the background (background effect).
It may be added here that the method might be improved by adding e. g. CaCO₃ to all the samples in order to obtain more constant conditions, or the samples could be diluted e. g. 10 times with Fe₂O₃. The dilution with Fe₂O₃ has been applied to the iron ores, and is a useful method.

An attempt was then made to find a comparison element which shows the same variations in intensity as V, when different compounds are added to the material to be examined. There was a possibility that Cr might be such an element, and a closer examination showed that Cr is a very suitable comparison element in this connection. The following will show this.

**How the Difficulties disappear when Cr is used as a Comparison Element instead of Fe.**

A good line was found in the Cr I-line 3034.190 which has no coincidences, and which is of a convenient intensity when Cr is present in amounts of about 10 per cent. The line pair V 3056—Cr 3034 must be considered well suited for the analysis and better than V 3185—Cr 3034, as the distance between the two latter lines is greater than generally desirable. The foregoing has also shown that the line V 3185 is subject to greater variations in intensity than V 3056, and therefore, though V 3185 is by far the stronger line, the chief interest was given to the line pair V 3056—Cr 3034. But the pair V 3185—Cr 3034 was also employed, and the results obtained by using this pair were good also.

The comparison element Cr was added to the samples, and to the standard mixtures in the form of Cr₂O₃, and in the proportion 10 parts of sample to 1 part of Cr₂O₃. To this mixture were added 2 parts of carbon powder as usual, and the working conditions were the same as previously described in this paper, with the exception that the electrodes were intensely preheated for 30 seconds before igniting the arc, in order to prevent spitting, which often occurs when this precaution is not taken.

To get a survey of the applicability of Cr as a comparison element, 1 part of Cr₂O₃ was mixed with 10 parts of each of the following standards (arranged in order of decreasing V-content):
SPECTROCHEMICAL DETERMINATION OF VANADIUM

A ..........(1.17 % \text{V})
B ..........(0.83 \% \text{V})
C ..........(0.50 \% \text{V})
B + Fe_2O_3 1 : 1
E ..........(0.23 \% \text{V})
D ..........(0.17 \% \text{V})

S_1 .......... \left( 0.117 \% \text{V} \text{ in synthetic slag} \left( \frac{V}{Fe} = 1.0 \% \right) \right)
S_1 + Fe_2O_3 1 : 1
S_2 .......... \left( 0.039 \% \text{V} \quad \rightarrow \quad \left( \frac{V}{Fe} = 0.333 \% \right) \right)
S_3 .......... \left( 0.0117 \% \text{V} \quad \rightarrow \quad \left( \frac{V}{Fe} = 0.1 \% \right) \right)

These standards have very different chemical compositions, the base substance varying from iron ore to slag containing about 60 \% CaO. But fig. 7 shows that the variations in base substance have only little influence upon the intensity ratio \( \frac{V}{Cr} \) of \( 3056 \) \text{nm} \( \rightarrow \) \( 3045 \) \text{nm}. The points belonging to the slags, ores containing rock minerals and mixtures of ores or slags with Fe_2O_3, all fall approximately on the prolongation of the calibration curve constructed for the iron ore concentrates A, B, and C. Thus instead of four or more calibration curves, which must be used when Fe is chosen as a comparison element, the determination of V with Cr as a comparison element can be carried out with the use of one single calibration curve, valid for concentrated and unconcentrated iron ores, and for slags of different compositions. The points in fig. 7 each represent the average of two different determinations. The deviations of the average values from the straight line are with few exceptions less than \( \pm 10 \) relative per cent, and those deviations are assumed chiefly to be due to some inaccuracy in the weighing or mixing of Cr_2O_3, when this is added to the standards. When the greatest accuracy is demanded, Cr_2O_3 should be added as a mixture of e. g. 20 \% Cr_2O_3 in e. g. CaCO_3 in the proportion 1 part of this mixture to 1 part of the standards as well as the samples to be analysed, as uncertainties of weighing are in this way considerably reduced.

How little the intensity ratio \( \frac{V}{Cr} \) of \( 3056 \) \text{nm} \( \rightarrow \) \( 3034 \) \text{nm} is affected by changes in the composition of the materials to be examined, is shown in table
3. It is seen that the addition of CaCO₃ has no great influence, and what is interesting too: If Cr₂O₃ is present in an amount of 1 percent instead of 10, this seems not to affect the result at all. By comparing the mixtures 1, 2, and 3 this is obvious.
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Table 3.

<table>
<thead>
<tr>
<th>Mixtures examined</th>
<th>log T in mm</th>
<th>Per cent of V in C</th>
<th>Actual V-content</th>
<th>V-content found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>Average</td>
<td></td>
</tr>
<tr>
<td>1 (C + Cr₂O₃ 10:1) + CaCO₃ 1:9 . . .</td>
<td>-5.5</td>
<td>-7.0</td>
<td>-6.3</td>
<td>0.50</td>
</tr>
<tr>
<td>2 (C + Cr₂O₃ 10:1) + CaCO₃ 1:1 . . .</td>
<td>-6.2</td>
<td>-6.2</td>
<td>-6.2</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Per cent of V in the mixtures in brackets

<table>
<thead>
<tr>
<th>Actual V-content</th>
<th>V-content found</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 (50% C + 50% CaCO₃) + Cr₂O₃ 10:1 . . .</td>
<td>-14.1</td>
</tr>
<tr>
<td>4 (8.5% A + 91.5% CaCO₃) + Cr₂O₃ 10:1</td>
<td>-28.0</td>
</tr>
<tr>
<td>5 (21.4% A + 78.6% CaCO₃) + Cr₂O₃ 10:1</td>
<td>-13.5</td>
</tr>
</tbody>
</table>

The fact that the presence of only one per cent of Cr₂O₃ in the material to be analysed is sufficient for a V-determination is very advantageous and can be utilized by the analysis of slags. Then the actual slags previously mentioned contain about one per cent of Cr₂O₃. If this Cr₂O₃-content is known, the V-determination is carried out without adding Cr₂O₃, and when the Cr₂O₃-content is unknown, both V and Cr₂O₃ are determined in one operation as follows: Spectra are taken of the slag with no extra Cr₂O₃ added, and of the same slag mixed 10:1 with Cr₂O₃. From the calibration curve are found the concentration ratios \( \frac{V}{Cr₂O₃} \) (a and b) for both samples, and the contents of V and Cr₂O₃ in the original slag are found from the equations:

I

\[
\frac{\% Cr₂O₃_{orig.}}{\% V_{orig.}} \cdot 100 = a
\]

II

\[
\frac{\% V_{mix.}}{\% Cr₂O₃_{mix.}} \cdot 100 = \frac{\% V_{orig.} \cdot \frac{10}{11}}{\% Cr₂O₃_{orig.} \frac{10}{11} + \frac{10}{11}} \cdot 100 = \frac{\% V_{orig.}}{\% Cr₂O₃_{orig.} + \frac{10}{11}} \cdot 100 = b
\]
i. e.

\[ \% V = \frac{a \cdot b}{10 (a-b)} \]

and

\[ \% Cr_2O_3 = \frac{10 \cdot b}{a-b} \]

in the original slag.

\( a \) is the concentration ratio \( \frac{V}{Cr} \) for the original slag and \( b \) is the concentration ratio \( \frac{V}{Cr} \) for the 10:1 slag—\( Cr_2O_3 \) mixture, both ratios in per cent.

In table 4 is as an example shown the determination of \( V \) and \( Cr_2O_3 \) in the slag 55 b, and the results are compared with the chemical data(6).

### Table 4.

<table>
<thead>
<tr>
<th>Material analysed</th>
<th>( \Delta \log T ) V-Cr in mm</th>
<th>( Cr ) in %</th>
<th>( % V )</th>
<th>( % Cr_2O_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag 55 b</td>
<td></td>
<td>-0.6 -0.9 -0.8</td>
<td>8.7 (a)</td>
<td>0.08</td>
</tr>
<tr>
<td>Slag 55 b + Cr_2O_3 10:1</td>
<td>-29.5 -29.2 -29.4</td>
<td>0.74 (b)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Summary.**

Two spectrochemical methods for determining vanadium in iron ores and in slags are described. By the first method the intensity of the V-lines 3185 and 3056 is compared with the intensity of the Fe-lines 3205 and 3055 produced by the Fe-content which the sample contained itself. Concentration-calibration curves were constructed by plotting the log exposure time ratios (\( \Delta \log T \approx \log \text{intensity ratio} \) \( \frac{V_{3185}}{Fe_{3205}} \) and \( \frac{V_{3056}}{Fe_{3055}} \) in mm against log concentration ratio \( \frac{V}{Fe} \). As standards were used chemically analysed iron ores and slags, and synthetic slags.

It is shown that the intensities of the V-lines applied are strongly affected by changes in the base substance, as \( CaCO_3, Al_2O_3 \), albite, labradorite, and olivine cause an increase of the V-line intensity. The rise in \( \Delta \log T \) produced by each of these compounds are quantitatively determined, and it is shown that the total increase in
$\Delta \log T$ produced by an albite—labradorite—olivine mixture can be calculated by adding up the partial rises produced by each of the component minerals. It is shown how the V-determinations, in spite of the variations in intensity due to changes in base substance, are carried out by using one separate calibration curve for each base substance.

By the second method 1 part of $Cr_2O_3$ is added for comparison to 10 parts of the standards and samples. The relative exposure time ratio $\frac{V}{Cr} \frac{3056}{3034}$ is plotted against log concentration ratio $\frac{V}{Cr_2O_3}$, and thus one single calibration curve is constructed, which is valid for iron ores and slags. It is shown that $\Delta \log T$ is very little affected by changes in base substance.

A method for determining V and Cr in slags spectrochemically by two spectra is described.

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