Measurement of Oxygen and Nitrogen in High Purity Metals Used as National Standards for Elemental Analysis in Germany by Classical Carrier Gas Hot Extraction (HE) and HE after Activation with Photons

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The special importance of the analysis of non-metals in high purity metals, which will serve as national standards for elemental analysis in Germany, is illustrated for oxygen and nitrogen. The typical range of the mass fraction of oxygen and nitrogen in these materials is below 10 µg/g, often close to 1 µg/g. The two methods applied at BAM for these measurements are classical carrier gas hot extraction (HE) and carrier gas hot extraction after activation with photons (PAA-HE). The approach, the methods and their advantages and limitations are discussed. Comparative results from the measurement of oxygen and nitrogen in Cu, Fe, Ga, Pb, Sn and W are presented.

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1. Introduction and Theoretical Aspects

At Bundesanstalt für Materialforschung und -prüfung (BAM) a system of national standards for elemental analysis is developed. At high metrological level this system aims at realising traceability of chemical measurement results to the SI units in Germany. In order to achieve small combined uncertainties according to GUM, high purity metals are used.

For the system of national standards in Germany two kinds of materials - type A and type B - are involved: Type B material, which is intended for matrix adaptation, will be certified for the absence of metallic impurities and is not of further relevance here. Type A material is intended to serve as an element amount standard and can be used for calibration in chemical measurements. For type A materials the mass fraction of the matrix element in a material needs to be certified. The final value for the mass fraction of the matrix element should carry a combined uncertainty below 0.0001. Since there is no analytical method to measure the mass fraction of a matrix element in a high purity material directly with sufficient small uncertainty, the mass fractions of all relevant impurities are measured, summed up and subtracted from the value of unity. Using high purity materials is advantageous, because a small absolute uncertainty for the certified value of the matrix element can be obtained.

Among the impurities, non-metals and especially oxygen are of special relevance, because they are often the main impurities and therefore introducing the largest uncertainty.

Looking at the impurity mass fractions it is important to make clear that it is the total mass fraction of an impurity which is of relevance for the intended application: thus, both, bulk as well as surface contributions must be taken into account, when the material is weighed on a balance for preparing a solution. This is different from e.g. material properties studies, where to a wide extent only the bulk content is of relevance. Values given on the final certificate are therefore only valid when a certain sample preparation is applied, including a certain cleaning procedure and retaining (observing) a certain geometry.

Most of the often very sensitive physical methods of measurement for oxygen and nitrogen require a calibration depending very much on the matrix. For our purposes this is not applicable, because 1) calibration materials do not exist for high purity materials and 2) because of reasons concerning traceability. Therefore, we have to follow the classical approach of decomposition of the sample, separation of analyte and matrix and final determination of the analyte by a method of measurement which can easily be calibrated. This is realised by carrier gas hot extraction.

2. Experimental

At BAM we apply two methods for the measurement of oxygen and nitrogen in metals. One is the classical carrier gas hot extraction (HE). A LECO 436DR analyser is used, which detects oxygen by infrared adsorption and nitrogen by thermal conductivity. Measurement parameters are optimised for the individual materials as described in Table 1. Calibration is performed by weighing solid compounds (KNO₃, Fe₂O₃)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Mass/g</th>
<th>Flux</th>
<th>Current applied/A</th>
<th>Heating time/s</th>
<th>Number of repeated determinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.8</td>
<td>—</td>
<td>850</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>Fe</td>
<td>0.8</td>
<td>—</td>
<td>850</td>
<td>60</td>
<td>4</td>
</tr>
<tr>
<td>Ga</td>
<td>0.8</td>
<td>0.27 g Ni</td>
<td>850</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>Pb</td>
<td>1.0</td>
<td>—</td>
<td>750</td>
<td>60</td>
<td>7</td>
</tr>
<tr>
<td>Sn</td>
<td>0.7</td>
<td>—</td>
<td>850</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>W</td>
<td>0.27</td>
<td>1 g Ni+ 0.1 g Sn</td>
<td>1050</td>
<td>60</td>
<td>10</td>
</tr>
</tbody>
</table>
of known purity and stoichiometry on a micro balance. Especially, as in the case for W, when the material under investigation gives a signal not different from the blank, it is important to check the recovery of the extraction process by addition of about 10µg O and N to the material. The blank resulting from crucible and eventually from flux material (Ni) used is taken into account.

The measurements on W were finally made on pieces of a rod 99.98% obtained from Alfa Johnson Matthey after etching twice according to BCR. In previous experiments tungsten rods of known purity and stoichiometry on a micro balance. Especially, as in the case for W, when the material under investigation gives a signal not different from the blank, it is important to check the recovery of the extraction process by addition of about 10µg O and N to the material. The blank resulting from crucible and eventually from flux material (Ni) used is taken into account.

The second and less commonly used method applied at BAM for the measurement of oxygen and nitrogen is carrier gas hot extraction after activation with photons (PAA-HE). In previous experiments tungsten powders with values for oxygen above 800µg/g were found to be unsuitable for our purpose.

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During activation, chemically activated oxygen from air reacts with the sample surface. This oxygen is also activated by PAA and must be removed before the decomposition. Therefore, etching is necessary and can be performed vigorously, because a possible re-oxidation with inactive oxygen is not disturbing the final determination. The vigorously etching is also the reason, why a special surface treatment before the activation is not necessary.

Due to the short half lives, sample and standard have to be measured at the same time, thus in different geometry.

3. Results and Discussion

Comparative measurement results for oxygen and nitrogen in different high purity metals obtained by HE and PAA-HE are given in Table 2. The values are in good agreement at a small level of uncertainty.

The case of oxygen in copper is an nice illustration that there is no correlation between the nominal purity and the total purity of a material. The copper material labelled B, which is of a nominal higher purity than the material labelled A, has an oxygen impurity far above 100µg/g. It would therefore not be suitable as a type A material. On the other hand this material is very suitable as a type B material, because of low metallic trace content. Moreover, from the case of the copper material labelled B it can be seen that the values for high concentrations obtained by PAA-HE usually carry larger uncertainties. However, one must keep in mind that the domain of PAA-HE is trace analysis and not determination of high concentrations.

For iron, the first candidate material for type A shows also
an oxygen impurity above 100 µg/g. The second material, a previously for some elements certified EURONORM CRM turned out to be suitable.

Oxygen and nitrogen values for Gallium seem to be rather high, since the purification technology for Gallium is highly developed, but must be seen in context with the specific sample preparation, which was melting the material under atmospheric conditions and transferring of the liquid via a pipette.

For the lead material labelled B the large uncertainty in the oxygen value is due to the geometry of the material, which is small spheres with cavities inside. Etching within these cavities cannot be performed with good reproducibility.

For copper labelled A, tin and tungsten, the oxygen values found do not differ from the blank value.

Except for iron and gallium, the nitrogen values are not different from the blank value. As in the case of oxygen, the large value for gallium is due to the sample preparation via pipette. The large uncertainty of the value for tungsten is due to an imperfect batch of nickel used as fluxing agent. This value can be improved.

Gallium, lead and tin could not be measured by PAA-HE up to now, since the samples get too hot during activation. Already in the case of lead (m.p. 600 K), errors due to melting at the surface of the sample during activation could not be fully excluded.

4. Conclusion

The measurement of oxygen and nitrogen is essential for the certification of national standards for elemental analysis in Germany, especially for type A materials. This is shown by sometimes surprisingly high values found for materials of high nominal purity. In contrast to e.g. materials’ studies, the measurand for our application is the total mass fraction of oxygen and nitrogen, not the bulk only. Due to the working principle, HE and PAA-HE give supplementary information. HE gives the total oxygen and nitrogen mass fraction, whereas PAA gives the bulk mass fraction only.

Since both methods are correlated in the carrier gas hot extraction step, a critical interpretation of the measurement results is required—even if good agreement is achieved between the values obtained from both methods.

REFERENCES