



## Arsenic in standard reference material 1571 (Orchard Leaves)

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*Publication date:*  
1973

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Damsgaard, E., & Heydorn, K. (1973). *Arsenic in standard reference material 1571 (Orchard Leaves)*. Risø National Laboratory. Risø-M No. 1633

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Danish Atomic Energy Commission

Research Establishment Risö

# CHEMISTRY DEPARTMENT

ARSENIC IN STANDARD REFERENCE  
MATERIAL 1571 (Orchard Leaves)

by

E. Damsgaard and K. Heydorn

Paper read at the  
3rd Symposium on the Recent Developments in  
Neutron Activation Analysis, Cambridge 1973

Risø - M - 1633

<p>Title and author(s)</p> <p>E. Damsgaard and K. Heydorn</p> <p>ARSENIC IN STANDARD REFERENCE MATERIAL 1571 (Orchard Leaves)</p> <p>Paper read at the 3rd Symposium on the Recent Developments in Neutron Activation Analysis, Cambridge 1973</p>	<p>Date July 4, 1973</p> <p>Department or group</p> <p>Isotope Division</p> <p>Group's own registration number(s)</p>
<p>7 pages + 2 tables + 3 illustrations</p>	
<p><b>Abstract</b></p> <p>Inability to attain the certified concentration of arsenic in National Bureau of Standards Reference Material 1571 prompted a detailed investigation of possible systematic errors in our method (1) for the determination of arsenic, manganese, and selenium in biological materials by neutron activation analysis.</p> <p>Possible shortcomings in analytical technique or housekeeping were scrutinized, and followed by careful investigation of more fundamental errors from</p> <ul style="list-style-type: none"> <li>Losses occurring before carrier addition</li> <li>Incomplete carrier exchange</li> <li>Interfering elements</li> </ul> <p>Results indicated that although our method was not entirely without systematic errors, their magnitude was insufficient to account for the discrepancy with the certified value.</p> <p>We are therefore led to conclude that the true concentration of arsenic in SRM 1571 Orchard Leaves is significantly lower than the <math>14 \pm 2</math> ppm certified by the National Bureau of Standards (2).</p> <p>Available on request from the Library of the Danish Atomic Energy Commission (Atomenergikommissionens Bibliotek), Risø, Roskilde, Denmark. Telephone: (03) 35 51 01, ext. 334, telex: 5072.</p>	<p><b>Copies to</b></p> <p><b>Abstract to</b></p>

The certification of trace element concentrations in Standard Reference Materials, initiated by the National Bureau of Standards, is of great importance because an analytical result should always be expressed with a realistic estimate of its accuracy. The precision of an analytical method may be found by analysing reference materials of unknown concentration, but the accuracy can be tested only by the analysis of materials for which the true concentrations are known. Therefore many of us rely on Standard Reference Materials from the National Bureau of Standards to test our accuracy.

We tested our routine analytical method for the simultaneous determination of As, Mn and Se in biological materials<sup>1)</sup>, by analysing samples of the National Bureau of Standard Reference Material 1571 Orchard Leaves, before the final certificate was issued<sup>2)</sup>. Later we learned that we had obtained good agreement with the certified values for Mn and Se, while an indisputable disagreement was observed for As. As our method had already been used for many determinations of As<sup>3)</sup>, we initiated a careful study to find the cause of the disagreement.

We found that although our method was not entirely without systematic errors, their magnitude was insufficient to account for the observed discrepancy.

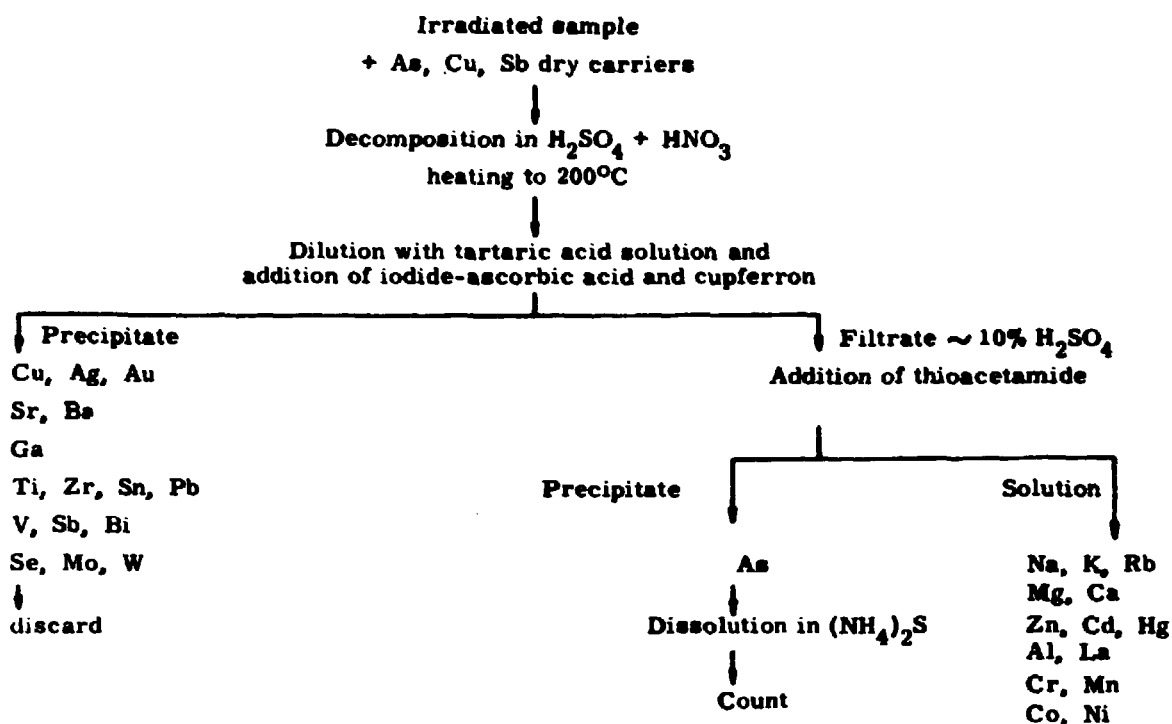
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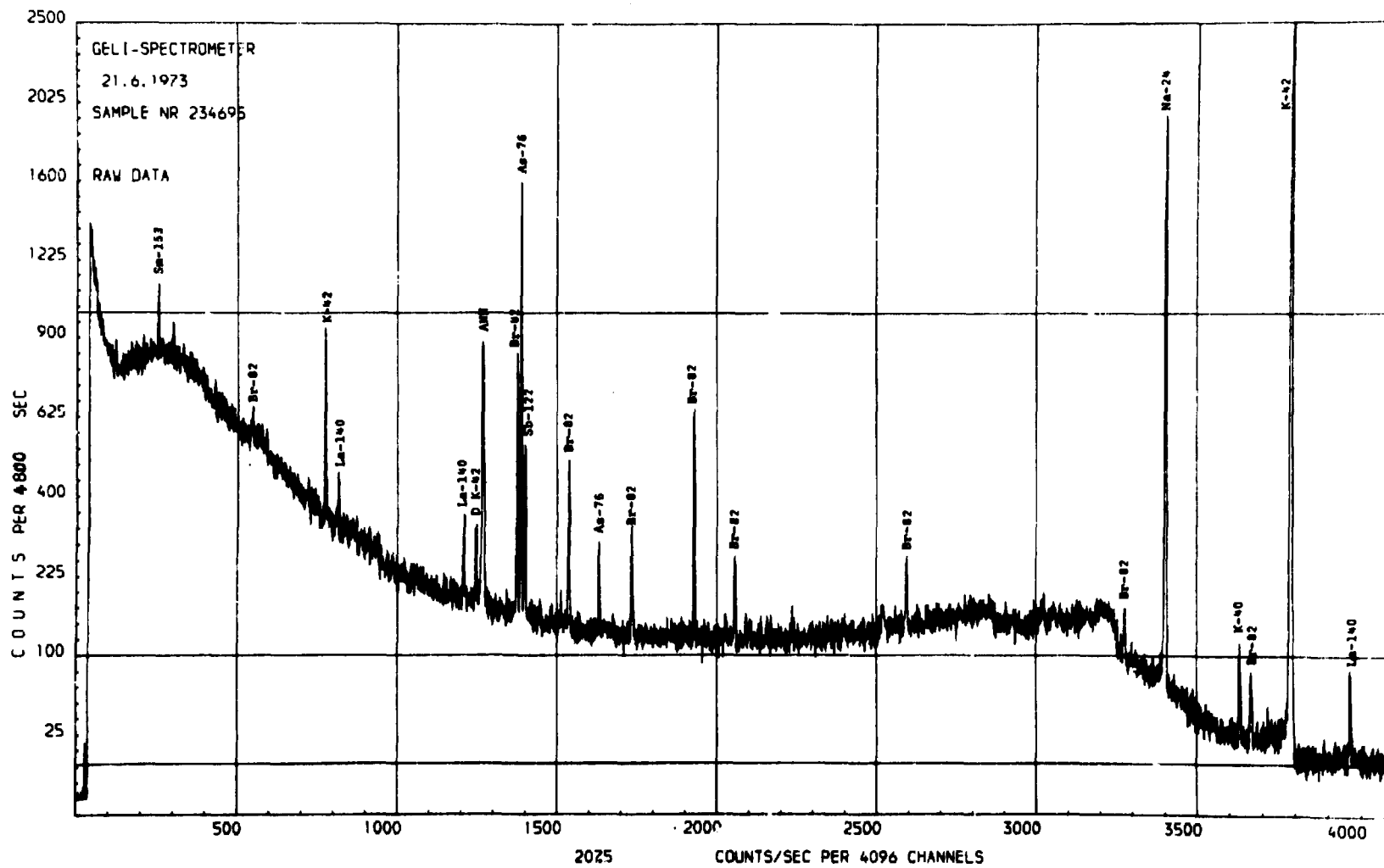
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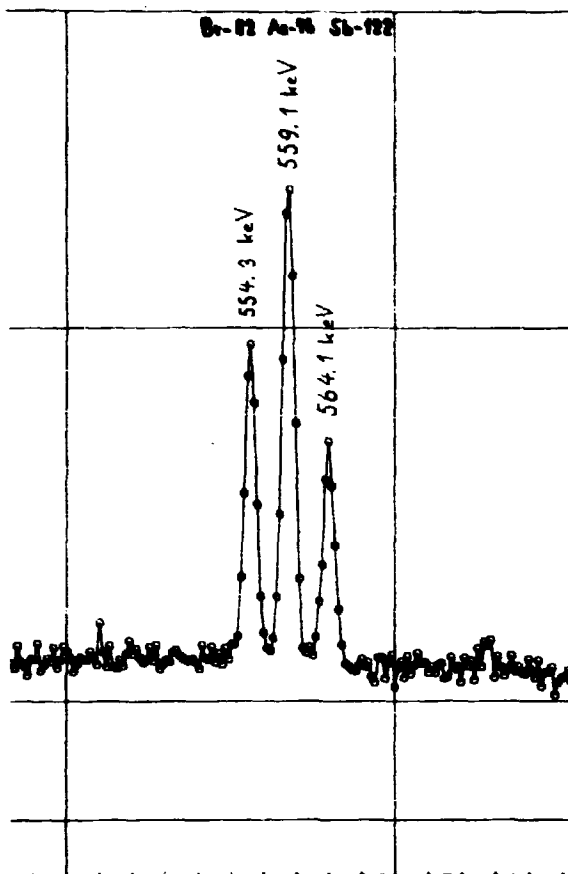


Our method is outlined on the first slide. After irradiation of the sample in the reactor, carriers are added, and the sample is decomposed in a  $H_2SO_4$ - $HNO_3$  mixture. We then perform scavenging, primarily to remove Cu and Sb, whereafter As is precipitated as sulphide. The precipitate is dissolved, and As-76 counted in a NaJ(Tl)-detector. The chemical yield of the separation is finally determined by re-irradiation.

The high arsenic concentration in SRM 1571 Orchard Leaves caused by accidental spraying with lead arsenate, makes the material amenable also for instrumental analysis by Ge(Li)-spectrometry. On the next slide, we see a spectrum of Orchard Leaves about 40 hours after the irradiation. All peaks are identified and none of the isotopes interfere with the As-peak at 559 keV. When we expand the region around the As-peak as we have done on this slide, you will see that the As-76 peak is surrounded by a Br-82 peak and an Sb-122 peak. However, the resolution is quite sufficient for interference-free determination of As; this was shown by stripping Br and Sb from the spectrum, leaving the area of the As-peak virtually unchanged.

Both of these methods, the determination of As after chemical separation and the determination of As instrumentally, were used in the investigation.





An obvious source of error would be a wrong value for our comparator standard. We store an aqueous solution with a concentration of 10 mg/ml of As, and its concentration was determined in 1966 not only by weighing the  $As_2O_3$  to be dissolved, but also by subsequent chemical analysis. This analysis was now repeated, and a deviation of less than 2% from the original value was found.

Comparator solutions of 10  $\mu$ g/ml are prepared with regular intervals by dilution with redistilled water, and when compared with their predecessor they usually agree within 1%.

Then we looked for possible shortcomings in our analytical technique. The error by pipetting the carrier was checked, and all reagents were analysed for possible As-content which could influence the chemical yield; neither was significant.



SRM 1577 BOVINE LIVER

Concentration of Arsenic

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	Mean value ppb	Number of determinations
This work	56.6 ± 1.2	6
NBS	55	preliminary

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Slide 4 confirms that our technique and method seem to work all right for the determination of As in the National Bureau of Standards SRM 1577 Bovine Liver. We obtained a mean value of 56.6 ppb in agreement with the provisional NBS value.<sup>4)</sup>

The investigation was now concentrated on the more fundamental errors: losses of sample arsenic, incomplete carrier exchange, and interfering elements.

Loss of As could occur:

1. during the drying of the material
2. during transfer of the irradiated material from the irradiation container to the beaker in which decomposition is carried out
3. during the ashing before carrier exchange has taken place

Losses after carrier exchange are unimportant as the chemical yield is determined later.

1. The orchard leaves were dried at 90°C as specified in the certificate<sup>2)</sup> and the loss was checked by analysing dried as well as not dried material. Taking into account a weight loss by drying of 5.86%, the results obtained were identical; a significant loss of As during drying was consequently ruled out.

2. Loss of As-76 during transfer of the irradiated orchard leaves to the beaker, which was used for the decomposition, was checked by counting a sample before the irradiation container was opened, and after transfer of the sample to an identical container. No loss was detected.
3. Still, losses during wet ashing remained a possibility: according to the analytical method, the decomposition of the irradiated sample is carried out in an open beaker. To catch possible volatile As compounds, the beaker was replaced by a closed system to trap the fumes and collect a distillate during ashing. The distillate and the trapped fumes were counted for As-76, and only insignificant amounts were found.

We believe that losses of As can be ruled out as a possible cause of our disagreement with the certified NBS value.

Our search was next concentrated on the question of incomplete carrier exchange, which results in an incorrect yield determination.

The degree of carrier exchange can be investigated by adding carrier-free As-74 as a tracer. The As-74 has a half-life of 18 days and a  $\gamma$ -energy of 596 keV, which is close to the 559 keV of As-76, but they are easily separated on a Ge(Li)-detector. This method is quite unique since we are now concerned only with the ratio between two peaks, two peaks with energies very close to each other.

In this way a measurement becomes independent of effects which usually have to be taken into account when making an instrumental determination, such as count rate and pile-up effects, gain and resolution change, variations in geometry and self-absorption; the precision depends only on the counting statistics.

This investigation was carried out in two steps:

1. a test for exchange between the As from the orchard leaves and the As-74 tracer.
2. a test for exchange between the As-carrier and the As-74 tracer.

In the first step, about 0.05 $\mu$ Ci of As-74 was added to a sample of irradiated orchard leaves, and the sample was processed according to the analytical method. Ge(Li)-spectra were taken of the sample before decomposition and after separation. The ratio between the As-76 peak and the As-74 peak was unchanged.

In the second step, the sample was composed of inactive orchard leaves, As-74 tracer and activated As-carrier. Again, the ratio between the As-76 and the As-74 peak was measured before decomposition and in the separated As-sample, and no difference was found.

These results verify that the exchange between As in the orchard leaves and the As-carrier is complete.

The last of the foreseen fundamental errors in our routine method was interference. Previous studies of the performance characteristics of the method<sup>1)</sup> included determinations of interference from other elements, and this information together with approximate concentrations of a number of elements given by the National Bureau of Standards rule out the possibility of serious interference.

We have now checked our routine method without finding serious systematic errors, but we know that the accuracy of the results will be improved if we use the As-74 tracer rather than re-irradiation for chemical yield determination.

SRM 1571 ORCHARD LEAVES

Concentration of Arsenic

	Mean value ppm	Number of determinations	Number of analysts
This work:			
Separation	9.7 $\pm$ 0.2	4	2
Instrumental	9.93 $\pm$ 0.13	12	2
NBS	14 $\pm$ 2	certified	3

The last slide shows our results for As in Orchard Leaves, when the radiochemical separation procedure is used in combination with Ge(Li)-spectrometry, and the yield is determined from recovered As-74. This referee reliable method gave 9.7 ppm which is not significantly different from the 9.93 ppm obtained by purely instrumental technique. Both results are, however, significantly lower than the NBS certified value of 14 ppm.

We have spent considerable time and effort in trying to get results in agreement with the certified value; we now hope that those among the audience who have analysed this material will comment on our findings and will help us locate the cause of our disagreement, or that the National Bureau of Standards reconsiders their certification and revises the current value for As in SRM 1571 Orchard Leaves.

1. K. Heydorn and E. Damsgaard, Risø Report No. 256 (1972) 143-61.
2. National Bureau of Standards Certificate of Analysis SRM 1571, Rev. Oct. 1, 1971.
3. N.A. Larsen, B. Nielsen, H. Pakkenberg, P. Christoffersen, E. Damsgaard, K. Heydorn  
Proc. Nucl. Act. Technique Life Sci., Bled (IAEA 1972) 561-68.
4. National Bureau of Standards Certificate of Analysis SRM 1577, Apr. 15, 1972.