DETERMINATION OF ARSENIC IN GERMANIUM BY THE COMBINATION OF ISOTOPE DILUTION AND ACTIVATION ANALYSIS

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The determination of arsenic by activation analysis in germanium may be disturbed by arsenic isotopes formed in the irradiation of the germanium matrix itself. The isotopic dilution technique will eliminate such interferences, but it requires weighing of very small masses of arsenic, after appropriate chemical separation. This weighing procedure can be avoided if the mass of the recovered arsenic is determined by activation analysis. In order to apply such a procedure, a known amount of arsenic labelled with $^{76}$As, whose specific activity is also known, is added to the germanium sample to be analysed. The sample is processed, the arsenic separated, and the chemical yield established. The recovered mass of arsenic is then determined by activation analysis applying the classical isotopic dilution analysis formula. The accuracy, precision and linearity of the method are discussed.

Introduction

Direct activation analysis without separating the element to be analysed before irradiation is not always possible. This applies, for instance, to the analyses of elements with atomic numbers from 30 to 64 in a uranium matrix, since these elements are formed by fission. Another instance where direct irradiation of the sample or matrix may not be advisable is when the matrix has a very high thermal neutron absorption cross-section, such as in the case of a gold matrix. Primary and second-order interference reactions, or any nuclear reaction in the matrix that may give rise to radioisotopes of the element being analysed, may also hamper direct activation of the samples.

Separation of the element to be analysed before irradiation may cancel the main advantage of activation analysis, which is insensitive to accidental contamination, as observed by Pauly, Sabbioni and Girardi. The loss of trace elements may also occur during separation prior to irradiation.

Application of the isotope dilution technique might by-pass the inconveniences concomitant of a direct irradiation of matrixes, such as the ones mentioned before, eliminating interferences due to fissile materials, high neutron absorption cross-section matrixes, and samples in which nuclear reactions between the matrix and bombarding particle may produce isotopes of the same element which is to be...
analysed. The isotopic dilution method also takes into account and corrects for any loss of the trace element being analysed. This method has already been applied, e.g., for the determination of traces of phosphorus in nuclear grade uranium. Although in this case the element to be analysed (phosphorus) is not a fission product, direct irradiation of the matrix would require remote control processing, owing to the high activity induced in the matrix due to the formation of fission products.

In isotopic dilution it is necessary to determine the specific activity of the isolated substance being analysed, and this requires the determination of its weight. Consequently, the sensitivity or the method will be highly dependent on this weight determination (gravimetry, spectrophotometry, etc.). Frequently, the amount of substance to be determined by gravimetry or some other procedure is very small, and a very sensitive method must be used. This high sensitivity may not always be attained by the usual chemical methods. PAULY, SABBIONI and GIRARDI have solved this problem by applying activation analysis for the determination of the weight of the recovered substance to allow the subsequent calculation of specific activity. The elements determined were lanthanum, cerium, ruthenium and molybdenum in a uranium alloy sample, for which direct irradiation is not possible since the mentioned elements would also be formed as fission products.

Conditions similar to those described above are encountered in the analysis of arsenic in germanium or germanium oxide. Germanium of high purity is required for the manufacture of diodes and transistors. The analytical methods used to check the purity of such material must have very high sensitivity. Activation analysis seems to be an extremely promising method for this purpose. In the case of arsenic, which is known to be one of the impurities that prevent such a use of germanium, activation analysis is more difficult than for the other contaminants, owing to matrix interferences. The interferences that may occur are indicated by Reactions (1) and (2).

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\begin{align*}
\text{\textsuperscript{76}}\text{Ge}(n, \gamma) & \rightarrow \text{\textsuperscript{77}}\text{Ge} \rightarrow \text{\textsuperscript{77}}\text{As} \\
\text{\textsuperscript{74}}\text{Ge}(n, \gamma) & \rightarrow \text{\textsuperscript{75}}\text{Ge} \rightarrow \text{\textsuperscript{78}}\text{As}(n, \gamma) \rightarrow \text{\textsuperscript{78}}\text{As}
\end{align*}
\]

\[\text{Reaction (1)}\]

\[\text{Reaction (2)}\]

DE SOETE, DE NEVE and HOSTE described a method for the activation analysis of arsenic in germanium, in which the activity due to \textsuperscript{77}As does not interfere with the measurement of \textsuperscript{76}As; they used the first reactions to establish an internal standard for the measurement of \textsuperscript{76}As. The second-order interference caused by Reaction (2) is discussed in detail by RICCI and DYER and by SMALES and PATE.