Determination of Selenium in the Environment and in Biological Material

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This paper reviews the following problems: sampling, decomposition procedures and most important analytical methods used for selenium determination, e.g., neutron activation analysis, atomic absorption spectrometry, gas-liquid chromatography, spectrophotometry, fluorimetry, and x-ray fluorescence. This review covers the literature mainly from 1975 to 1977.

Introduction

Selenium is widely distributed in the environment (waters, soil, and air) albeit generally in very low concentrations ($\leq 1 \mu g/g$). The selenium content sometimes reaches 0.5 mg/g in limonite rocks, and 2.6 mg/g in vanadium-uranium rocks. Data on selenium-containing rocks are from North and South America, Canada, Columbia, Mexico, Australia, New Zealand, Ireland, Bulgaria, Germany, USSR and Mediterranean countries. Some waters were also reported to contain elevated concentrations of selenium, e.g., Colorado channels or subterranean waters in the region of Orsk.

Selenium and its compounds have found broad technological applications, among others in electronics (for production of semiconductors, photo-cells, and rectifiers), machine industry (for obtaining high-grade steel), glass industry (for staining of glass), chemical industry (as a catalyst), rubber industry (for acceleration of vulcanization), and pharmaceutics (veterinary selenium preparations in treatment of diseases due to selenium deficiency). In agriculture, organoselenium compounds are used as bactericides, fungicides, and herbicides.

This broad technological application brings about growing selenium pollution of the atmosphere. For example, in the U.S., the yearly emission of selenium compounds into the atmosphere amounted to 1,000 tons, i.e., 0.14% of the total emission of metallic compounds. In England, the atmospheric concentration of selenium almost doubled in the years 1957-1974. Since the 50's it has been known that selenium is one of the elements indispensable for normal plant growth and functioning of animal organisms. Nutritional selenium deficiency results, in muscular dystrophy and liver necrosis. At present, sodium selenite is used at doses far below toxic in many countries in breeding farms for prophylactic and therapeutic purposes. The nutritional requirement for selenium has been stated by Scott to lie in the range 0.1-0.3 mg/kg, whereas levels from 2 to 10 mg/kg give rise to chronic toxicity symptoms. Apart from the overall beneficial biological role of selenium it was established that this element plays a protective role in poisoning with heavy metals (Hg, Cd, As, and Tl). Therapeutic selenium doses applied in these cases are close to toxic (LD$_{50}$ for the rat is 3 mg/kg).

The toxicity of selenium and its compounds is high. Oral administration of inorganic and organic selenium compounds results in various forms of cancer. In 1970 selenium, as a causative of liver carcinoma, was included into the list of a few inorganic carcinogenic agents. Moreover, selenium compounds cause cirrhosis, teeth and hair loss, and paralysis. In as early as 1560, chronic human selenosis was described in South America,

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and cattle diseases, so-called alkali disease and blind-staggers, have long been known in North America. The maximal permissible concentration of selenium in water and liquid wastes established by WHO is 10 μg/l. According to Rosenfeld (1), concentrations of 5 μg Se/g in food and 0.5 μg Se/g in milk and water form a potential danger for humans.

In spite of the well-known toxic effects of selenium, this element has not been acknowledged enough as a pollutant for a long time. This situation was changed after inclusion of selenium in a list of carcinogenic agents. Since that time many papers appeared devoted to determination of selenium in the environment and biological material. This field has been reviewed by Masson (8), Shendrikar (9), Zingaro and Cooper (10), and Crosby (11), but he reviews (8, 9) and a monograph (10) cover literature up to 1974. In view of the profound recent interest in selenium and its role in the environment, reviewing modern analytical methods of determination of this element seemed worthwhile.

**Sampling**

Sampling of biological material for determination of selenium does not usually pose a problem. Care must be taken only that samples be representative. The case of urine is somewhat different. Cornelis et al. (12) emphasized the importance of the method of sampling, preparation, and storage of urine. They advised sampling as soon as possible into ultrapure polyethylene vessels in which all the subsequent operations (freeze-drying, irradiation) necessary for estimation of selenium by neutron activation analysis could be performed. Such a procedure considerably decreases the danger of contamination. One should take into account, however, that storage of aqueous solutions of selenium results also in losses (13), depending on the composition, of the container walls and pH of the solution. For polyethylene containers, the losses of a 1 ppm Se solution during 2-week storage amounted to 8.3% and 2%, respectively, for pH values of 7 and 3.8. Water sampling usually involves only filtration and concentration due to a low content of selenium (10⁻⁹ g/cm³).

Air sampling for monitoring of selenium content is a difficult question due to the volatility of its compounds. These compounds can occur in gas, liquid, and solid states. Their vapor pressure is high enough to exclude filtration as a routine method of air sampling. There are few data in the literature concerning this question (8, 14). Pillay et al. (15) used sequential tape sampling and found that on the average, 56% of selenium could not be retained by filter tapes. Nevertheless, filters [Whatman No. 41 (16) and 542 (17), Mikrosorban SM 159 (16), Millipore (14, 18) and Fiberglas (14), Delbag polystyrene (16)] and sometimes liquid impingers (14, 19) have been most frequently used for air sampling.

Maenhaut and Zaller (17) compared sorptive properties of Whatman No. 542 cellulose filters and 0.4 μm Nucleopore polycarbonate filters in estimating 35 elements, among them selenium. For the latter, the ratio of the amounts collected on Whatman and Nucleopore filters was 0.0078, evidencing much better sorptive properties of 0.4 μm Nucleopore filters for selenium and selenium compounds than of Whatman No. 542 filters.

Arguments in favor of use of the impingement technique provided by Shendrikar and West (14) seem quite convincing. These authors compared the efficiency of sampling of airborne selenium by using filtration and impingement techniques and found a considerable (19–38%) loss of selenium upon filtration through Fiberglas or Millipore filters. This loss was further augmented with increasing volume of the sample. The authors recommended absorption in water as the most efficient route of selenium sampling from the air. Water is the best absorbent for selenium due to the high water solubility of selenic and selenious acids formed in the presence of moisture from selenium oxides.

**Decomposition Procedures**

There are many methods of decomposition of samples for the determination of selenium in the literature, as shown in Table 1 (20-55). This question has been discussed thoroughly in several papers (8-10, 56, 57). Wet oxidation of samples was used in the majority of cases due to selenium losses in the dry ashing method and limitations of sample size in the oxygen flask technique. The most popular methods involve digestion with HNO₃, HClO₄, H₂SO₄, and H₂O₂ mixtures. Concentrated HCl was avoided, as selenium forms volatile adducts with chloride (e.g., SeOCl₂, SeO₂·2 HCl). The main difficulty in wet oxidation procedures lies in prevention of volatilization of selenium. The simplest solution is lowering of the mineralization temperature, but this involves prolongation of the time of mineralization. Selenium is also prone to reduction to volatile derivatives if reducing conditions occur during sample mineralization (charring). Charring usually takes place (57) when oxidizing mixtures containing sulfuric acid are used. This results in forming charred residue, which is treated next with another oxidant (HNO₃, H₂O₂) which continues the decomposition by further oxidizing of the partially degraded fragments. In order to prevent selenium loss and maintain oxidizing conditions throughout
Table 1. Methods for decomposition of materials containing selenium classified by final determination method.a

| Digestion mixture | Nuclear activation analysis (NAA) | Atomic absorption spectroscopy (AAS) | Fluorimetry | X-ray fluorescence analysis (XFA) | Gas-liquid chromatography (GLC) | Other |
|-------------------|----------------------------------|-------------------------------------|-------------|----------------------------------|-------------------------------|-------|
| HNO₃-H₂SO₄        | (20, 21)                         |                                     |             | (22, 23)                         | (32)                          |       |
| HNO₃-HClO₄        |                                 |                                     |             |                                  |                               |       |
| HNO₃-H₂O₂         | (33)                             |                                     |             |                                  |                               |       |
| H₂SO₄-H₂O₂        | (34)                             |                                     |             |                                  |                               |       |
| H₂SO₄-HClO₄       | (35)                             |                                     |             |                                  |                               |       |
| HClO₄-H₂O₂        | (36)                             |                                     |             |                                  |                               |       |
| HNO₃-H₂SO₄-H₂O₂   | (37)                             |                                     |             |                                  |                               |       |
| HNO₃-H₂SO₄-HClO₄  | (24, 38, 39)                     |                                     |             | (40, 41)                         |                               |       |
| H₂SO₄-H₃PO₄-HNO₃  | (42)                             |                                     |             |                                  |                               |       |
| HNO₃              |                                  |                                     |             | (43–45)                          | (46)                          | (48)  |
| HNO₃ + Mg(NO₃)₂   | (49)                             | (50)                                |             |                                  |                               |       |
| Dry ashing        |                                  |                                     |             |                                  |                               |       |
| Oxygen flask combustion | (51, 52)                 |                                     |             |                                  |                               |       |
| Molybdate mixtures| (22, 54)                         | (44, 55)                            |             |                                  |                               |       |

a Values are literature references.

The mineralization procedure, mixtures with HClO₄ are used most frequently.

The choice of an appropriate decomposition method should be made by taking into account the final method used for the determination. For determination of selenium by gas chromatography, 2 hr mineralization with nitric acid at 150°C [(animal tissues (43, 44)) or 170-180°C [(plants) (45)] is often used with success. Special care has to be exercised to prevent the formation of a charred material by frequent shaking. The excess acid is removed by heating of samples for 10 min with 1M urea solution, decomposing into nitrogen oxides.

Holyńska and Lipińska-Kalita (22) tested two procedures (23, 58) of mineralization employed for determination of selenium in biological material for x-ray fluorescence analysis, using the 77mSe radio-tracer. They found that selenium losses during mineralization do not exceed 5% for the HNO₃-H₂SO₄ mixture and 1% for the H₂SO₄-HClO₄-molybdate mixture. The latter method provided, however, a much higher recovery of selenium in the precipitate (94.6 ± 4.2% versus about 50%). It should be mentioned that the mineralization with sodium molybdate is rapid, requiring only about 1 hr at 160°C.

**Analytical Methods**

A variety of analytical methods can be applied for determination of trace amounts of selenium (ng/g) in various materials. In recent years (1975–1977) they included mainly: neutron activation analysis, NAA (35%); atomic absorption spectroscopy AAS (22%); gas chromatography, GLC (12%); spectrophotometry (4); x-ray fluorescence analysis (4); and others, among them fluorimetric and potentiometric methods (19). A lot of data concerning environmental analysis water (59) and air (60, 61) including selenium have been given in periodical reviews.

**Neutron Activation Analysis (NAA)**

Owing to the high detectability (10⁻⁸–10⁻⁹g Se) this method is widely used for determination of selenium in biological material as well as in the environment. Activation with thermal neutrons (E ≤ 0.2 eV) is performed most frequently, as they are a source of radioactive selenium isotopes in (n, γ) reactions (Table 2). Among the latter, only 77mSe and 75Se are presently utilized in activation analysis. 77mSe, providing the highest sensitivity thanks to a very short half-life (17.5 sec) is employed only in instrumental neutron activation analysis (INAA). 75Se is used most frequently, as its long half-life time (120.4 days) allows for chemical separation; however, long activation times are required.

The examined material is usually irradiated in a nuclear reactor with a flux of 10¹³–10¹⁵ n/cm²·sec for 7–14 days (for 75Se) or several seconds (for 77mSe). The activity of the irradiated samples is measured with a γ-ray multichannel analyzer and high-resolution Ge/Li (or sometimes NaI/Tl) detectors.

The most popular standard reference samples in biological studies are bovine liver, Bowen's kale, and orchard leaves, and in environmental studies coal and water (N.B.S.). Nadkarni and Morrison (63) proposed application of standard reference materials as multielement standards and tabulated reference element content of four popular standards.
Many data concerning application of NAA in biological and environmental analysis are contained in recent reviews (64, 65).

Biological Samples. Both the radiochemical (NAA) and instrumental (INAA) variants have been used (Table 3) (4, 16-18, 20, 21, 35, 37, 42, 49, 51, 63, 65-111).

Radiochemical separation methods are based on precipitation of selenium (20), separation on aminexchangers (66) and, most frequently, distillation (35, 89, 98, 112) and extraction (35, 98, 113). Byrne and Kosta (67, 114, 115) described a convenient method of simultaneous determination of mercury and selenium in biological samples pyrolyzed in a stream of oxygen and found (67) a correlation between the levels of mercury and selenium in humans exposed to inorganic mercury.

Zmijewska and Semkow (35) extracted selenium with benzene containing 1% phenol or distilled it from a HBr–HCl medium following mineralization of material with a H2SO4–HClO4 mixture. They found that distillation is more time-consuming than extraction. After distillation, the selenium recovery and detectability limit were 98.4% and 2 ng, respectively. The selenium content was, e.g., 0.66–0.84 μg/g in the serum.

Hoede et al. (21) determined selenium in chicken feed after its dissolution in a H2SO4–HNO3 mixture and toluene extraction. An advantage of this method consists in a possibility of determination of both Se (IV) and Se (VI).

Steinnes (42) reported a scheme for separation of 11 trace elements in biological material. He oxidized samples with a H2SO4–H3PO4–HNO3 mixture, distilled selenium, arsenic, and mercury in the presence of HCl and HBr, and precipitated selenium with thioacetamide. The distillation residue was extracted with a cyclohexanone solution of triethylphosphine oxide, and Mo, Ca, Cd, Zn, Fe, Co, and W were determined in the extract. Automatic methods were also elaborated for determination of selenium and other elements in biological material (66, 116) based on mineralization of samples with mixtures of different acids, selective distillation of volatile elements (among them selenium), and ion-exchange chromatography.

Nagy et al. (37) proposed a semiautomatic radiochemical method of determination of volatile elements consisting in oxidation of samples with a H2SO4–HNO3–H2O2 mixture, bromination and chlorination. This method permits determination of As, Se, Br, Sn, and Te (separation time: 215 min).

For determination of selenium, a nondestructive

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variant of instrumental neutron activation analysis (INAA) was used more frequently. Girardi (69) presented typical applications of INAA for studies of prolonged low-dose exposures in vivo to different compounds (rats) and in vitro experiments. In the same way Persigehl et al. (70) determined the content of Fe, Zn, Rb, Co, Cr, Se, Sc, Sb, Cs, Al, and Eu as trace elements in human tissues as a function of age of individuals. Jurgensen and Behne (71, 72) studied changes of the content of Br, Cs, Na, Rb, Se, and Zn in human blood serum (0.086-0.125 μg Se/g), and Schelenz (117) and Clemente et al. (80) determined the content of trace elements (Se) in human food.

Brötter (79) estimated the content of 25 elements in huma skeleton. Cornelis et al. (12) determined 16 elements in human urine. The urinary levels of selenium were: 27 and 19.5 μg/g in females and 90 μg/g in males.

Nordheim and Steinnèes (73) estimated the content of Zn, Cd, Hg, Cu, As, and Se in protein fractions of human liver combining INAA with Sephadex G-75 chromatography.

Vobeczky et al. (74) elaborated an INAA variant for submicrogram amounts of selenium in rat diet (0.07 μg/g) using activation with epithermal neutrons and multidimensional detection of 76Se. Advantages of this method are: short "cooling" period (adjusted to a decay of such short-living isotopes as: 24Na, 76As, 125Sb, or 140La) and possibility of analysis of complex matrices forming isotopes emitting radiation that interferes with the analytical lines of 76Se.

Diksic and McGrady (75) and McKown and Morris (76) used the 77mSe isotope for INAA of biological samples. Prior to irradiation tissues were freeze-dried (76) in order to reduce the amount of 19O. This method is suitable for analysis of all human and animal tissues except for skeleton.

Human hair is frequently used as an index of human exposure to environmental metals or for identification in criminology. Usually single hairs are analyzed by INAA. Dybczynski and Boboli (81) estimated the content of Ag, As, Au, Br, Cu, Hg, Zr, La, Mn, Na, Sb, Se, Sr, and Zn in single human hairs. Pillay and Kuis (82) determined 21 elements (among them Se) in human hair (average content of selenium: 1.3 μg/g). These authors indicated potential possibilities and limitations of INAA in providing forensic evidence. The limitations are due mainly to the large number of data needed for statistical analysis of results. The content of many elements (among them Se) was estimated in hair in the Upper Silesia Industrial District by Dutkiewicz et al. (83) and in Hong Kong by Chuang and Emery (84) for environmental monitoring.

Huang et al. (49) elaborated a radiochemical method of analysis of a set of elements in ashed hair avoiding interference from 82Br and 38Na. The ash is dissolved in hydrochloric acid and run through a Sb2O5 column to remove 24Na. In this way theoretical recoveries can be achieved for Ag, As, Au, Cd, Co, Cu, Fe, Ga, In, La, Mn, Ni, Sb, Se, Sr, and Zn.

Brune and Videred (77) compared activation by epithermal and thermal neutrons in analysis of trace elements (As, Br, Cd, Cu, Fe, Mn, Mo, Na, Se, and Zn) in biological material. They found that application of epithermal neutrons leads to formation of lower amounts of 24Na, and so this method is especially suitable for analysis of sea water. Values of the so-called "advantage" factor were > 1 for all the elements, among them Se (14.6) in the case of epithermal neutrons.

Water. The method of INAA is frequently used for estimation of water pollution. In the majority of cases concentration of water was performed before determination. Separation of the elements to be determined is often needed, too. Dybczynski et al. (99) discussed in detail the questions of accuracy and precision in determination of trace substances in water. Massee et al. (100) estimated selenium in fresh and sea water (0.16 and 0.13 μg/l, respectively) using preliminary filtration or centrifugation, reduction of selenites to metallic selenium with ascorbic acid and adsorption of selenium on active carbon. They determined also Se (VI), down to 10 ng/l., after reduction of selenites to selenites. This method allows estimation of Se (IV) and Se (VI) in 40 samples daily. Lieser et al. (101) also employed carbon adsorption (in the presence of chelating agents) for determination of Ag, Au, Cd, Ce, Co, Cr, Eu, Fe, Hg, La, Mo, Sc, Se, U, and Zn in sea water (0.63 ng Se/l.). Schutyser et al. (118) estimated 35 trace elements in rain water (3 ng Se/l.) while Lieser and Neitzert (119) analyzed river (0.7 ng Se/l.) and drinking water in Darmstadt (1.1 ng Se/l.).

Clemente and Mastini (98) proposed a rapid INAA method of determination of trace elements (Na, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Br, Rb, Ag, Sb, Cs, W, and Hg) in natural and contaminated waters needing neither separation nor concentration. By INAA Miklishanskii et al. (102) determined the content of 29 trace elements (10−5−10−2%) in Antarctic snow, and Kosta et al. (103) determined trace elements in Adriatic waters, in tissues of animals from the region of Rijeka and in marine invertebrates from the Slovenian coast. Nadkarni and Morrison (104) estimated 47 elements in lake sediments (0.08–1.01 μg Se/g) using radiochemical separation for seven noble metals and INAA for the remaining elements.

Air. In studies of air, INAA was employed
most frequently. Kronsborg and Steinnes (105) elaborated a method of determination of air pollution enabling simultaneous estimation of Sc, Cr, Fe, Co, Zn, Se, Ag, and Sb.

Obrusnik et al. (106) determined the content of various elements in fly-ash (64 ng Se/g) and industrial emissions and Dams et al. (107) as well as Vogg and Hartel (108) in urban aerosols. Dams et al. (109) employed $^{75}$Se for estimation of Se along with F, Sc, Ag, and Hf in urban and industrial aerosols. Interference from other elements was prevented by irradiation of samples through a cadmium shield.

Olmez and Aras (16) proposed a complex analytical scheme for determination of 30 elements from atmospheric pollution employing photons, thermal and 14 MeV neutrons. Among others, they estimated selenium in several cities obtaining values of 116, 1.4, and 19.2 ng Se/m$^3$ for Ankara, Boston, and Osaka, respectively.

Rowe and Steinnes (110, 111) determined 30 elements in coal and fly ash (10.8 µg Se/g) using activation with epithermal neutrons for Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, Cs, Ba, Sm, Tb, Hf, Ta, W, Th, and V, and with thermal neutrons for Sc, Cr, Fe, Co, Nd, Eu, Yb, and Lu.

A radiochemical variant of NAA was employed by Miyama and Lima (18) and Wilshire et al. (51). They (18) converted Hg, As, Sb, and Se collected from air into bromides with a 40% HBr-HNO$_3$ mixture (1:1). Then the bromides were dissolved in a hot H$_2$SO$_4$-H$_2$O$_2$ (8:7) mixture and redistilled (59).

Wilshire et al. (51) estimated the content of heavy metals (Hg, Zn, Cd, As, and Se) in coal and fly ash. Irradiated samples were combusted at 1200°C, trapped in liquid nitrogen and extracted with a 10% xylene solution of triisooctylamine. Selenium and arsenic were then estimated in the aqueous layer.

**Soil.** In studies of soil, fertilizers and rocks, radiochemical variants of NAA were usually employed. In this way Kronborg and Steinnes (94) estimated selenium (0.2–1.6 µg/g) and arsenic (0.5–7 µg/g) in soils and Mignonsin and Roelands (95) as well as Artemiev and Stepanov (91) determined (0.14–1.1 µg/g) and tellurium in geological samples.

Wilshire et al. (51) determined some elements (As, Cd, Hg, Se, I, and Zn) in environmental samples, which after combustion were extracted with 10% xylene solution of triisooctylamine. It should be mentioned that liquid samples can be measured in this way using simply extraction without combustion. Orvini et al. (52) elaborated a method for simultaneous determination of Se, As, Zn, Cd, and Hg, in environmental samples based on combustion in a stream of oxygen, heating up to 1180°C in a stream of carbon monoxide and condensation at a liquid nitrogen temperature. The estimated metals were precipitated as sulfides to avoid interference from $^{82}$Br. Wiseman and Bedri (120) determined heavy metals and selenium in fertilizers using a radiochemical separation (reversed phase anion paper chromatography) for analysis of Se, Hg, and Cu.

Zmijewska and Semkov (35) estimated the selenium content of soil and furnace waste dumps employing extraction of this metal with benzene containing 1% phenol. They obtained values of 0.10–0.18 and 1.50–4.55 µg Se/g for the soil and ashes, respectively. Van der Klugt et al. (96) determined the content of 41 elements in soil (1.36 µg Se/g) using INAA and computer elaboration of results.

In order to increase the sensitivity of determination, Baedecker et al. (97) employed epithermal analysis for instrumental analysis of 23 elements (among them Se) in silicate rocks. Ryan et al. (85, 87) described a rapid, sensitive and relatively cheap method of INAA for multielemental analysis of different samples (as water, wastes, hair, blood and coal dusts) using a Slowpoke reactor that seems very promising for environmental monitoring.

**Atomic Absorption Spectroscopy (AAS)**

This method, which has found a broad application for determination of many metals in the environment (Table 4), in its classical form is not enough sensitive for determination of selenium. The most intense resonance line of selenium (196.03 nm) corresponds to a range near to the vacuum ultraviolet. Moreover, the most frequently applied air-acetylene flame absorbs about 55% of radiation intensity of the light source. When using electrode less discharge lamps (EDL) and air-acetylene flame, a lower detectability level of 0.2 µg/ml can be reached that can be extended down to 0.1 µg/g by application of a deuterium lamp for background correction. The argon-hydrogen flame is often used for augmentation of sensitivity but it increases interferences, too. Extraction (121) was also attempted for improvement of sensitivity but in selenium determination a reextraction to a water solution was necessary.

Flameless atomic absorption (FAAS) techniques offer a high sensitivity ($5 \times 10^{-11}$ g Se) but are not simple nor free from interference, due to the high volatility of selenium. FAAS is suitable especially for direct analysis of samples and its additional advantage lies in possibilities of "chemical treatment" of samples in the graphite sample cell in order to diminish chemical interference.
tions of FAAS for environmental analysis of metals have been reviewed by Dokiya et al. (122).

It was revealed that addition of nickel (24, 33, 53) or cobalt salts (34) enhances significantly the sensitivity for selenium (by about 30%) and allows higher ashing temperature (1000°C) without losses. In the presence of these metals, no interference was observed from other elements capable of formation of selenides, viz., Ba, Cu, Fe, Mg, and Zn, and interference due to the presence of As was diminished significantly. A similar effect was also noted in the presence of molybdenum salts (33). Montaser and Mehrabzadeh (144) reached a detectability level of $1 \times 10^{-12}$ g selenium using graphite electrothermal furnace and background correction with a deuterium lamp.

In the last years, a growing interest is observed in the technique of hydride generation (HGAA) for determination of many metals (among them selenium). This technique is more and more popular in laboratories estimating trace metals in materials of changeable composition, as the graphite furnace method is often not reliable due to the strong and variable matrix effect and signal splitting. The hydride generation method consists in measurement of atomic absorption (or, more rarely, emission) of selenium hydride formed as a result of reduction of selenium and its compounds [Se (IV)] with different reducing mixtures Zn-SnCl$_2$-KI (145) or, usually, NaBH$_4$ (25, 26, 36, 38, 39, 50, 134-137, 146-148). HGAA techniques are more sensitive for detection of selenium than classical flame ionization by three orders of magnitude, the detectability limit amounting to 0.2 ng Se/g. They have an additional advantage of separating selenium from the matrix before atomization thus avoiding interferences inherent to the conventional technique (129, 149, 150). Practical analytical working ranges for selenium (151) are 3-250, 0.03-3, and up to 0.12 μg/ml, respectively, for flame atomic absorption, furnace atomic absorption, and vapor generation methods.

Pierce and Brown (146) studied the effect of interference in determination of arsenic and selenium by automatic HGAA. They recommended addition of hydrochloric acid prior to NaBH$_4$ in order to decrease the interferences from 24 ions. The influence of HCl concentration in the sample solution on the interferences was also emphasized by Meyer et al. (152). Pierce and Brown (147) compared the sensitivity and effects of different inorganic interferences in three techniques of determination of arsenic and selenium: manual hydride generation coupled with atomization in the argon-hydrogen flame, automated hydride generation with quartz tube atomization, and graphite furnace atomization and recommend the automated evolution technique as the method of choice.

**Water.** The method of AAS is well suited for analysis of various types of water. This field has been extensively reviewed by Fishman and Erdman (59), and Dean and Rains (153). Mesman and Thomas (130) compared the flame and graphite atomization methods of determination of selenium and arsenic in water from the viewpoint of speed, sample size, potential interference, variation coefficient, and general simplicity.

Henn (33) elaborated a sensitive FAAS method for determination of selenium (1-50 μg/l) in waters and industrial effluents using a preliminary purification on cation-exchange resins, combustion according to EPA and addition of molybdenum salts.
(100 mg/l.) for augmentation of sensitivity, increase of ashing temperature, and diminution of interference. This technique was also used by Martin et al. (131) for estimation of selenium in fresh water, wastes, sediments, and muds by using combustion with a HNO3-H2O2 mixture with addition of Ni(NO3)2 to prevent selenium losses during ashing and obtained a detectability limit of 0.2 µg/l. Kamada et al. (132) revealed interferences when estimating As, Sb, and Se in river and polluted waters by FAAS in the presence of acids (HCl, H2SO4, and HNO3). Kamada et al. (133) proposed a simple method of determination of Se (IV) and Se (VI) in different waters with carbon tube atomizer. Immediately thereafter, the sampling water was acidified to pH 1 and selective extraction with sodium diethylthiocarbamate and CCl4 was carried out for estimation of Se (IV). The content of Se (VI) was determined as the difference between the total Se and Se (IV) content. The detection limit was 0.4 ng Se/l. The Se (IV) and Se (VI) levels were 20, 12, and 21 and 0.36 and 18 ng/l, respectively, for river water, wastes and sea water.

McDaniel et al. (154) elaborated a procedure for concentration of selenium from environmental samples and determination in a graphite furnace (0.1–2 µg Se/50 ml) employing extraction, electrolysis, coprecipitation, and generation of selenium hydride but the calibration curve obtained was nonlinear.

For determination of selenium in water, the method of hydride generation was used most frequently in combination with either detection in Ar-H2-air flame (134, 135, 137) or FAAS (136, 138, 139, 143, 146). Corbin and Barnard (137) estimated inorganic compounds of arsenic and selenium (down to 0.01 µg/l.) in water after mineralization, while King and Morrow (137) applied this method to a direct determination of selenium and arsenic in surface waters with a detection limits of 5 µg As/l., and 1 µg Se/l.

Goulden and Brooksbank (134) put forward an automatic HGAA method of for determination of As, Sb, and Se in natural waters using detection in Ar–H2-air flame. They performed preliminary removal of NO3– ions by heating of samples with K2SeO3 and HCl until boiling. This method enables determination of 40 samples daily with a detection limit of 10.1 µg/l., for selenium and arsenic and 0.5 µg/l., for antimony.

Kunselman and Huff (143) applied HGAA combined with FAAS for direct determination of As, Sb, Se, and Te in industrial and sewage effluents. In a similar manner, Dujmovic (138) estimated selenium and arsenic in water but measured the generated hydrides in an electrically heated quartz tube. He found that organic contaminations present in water can be easily removed by irradiation with ultraviolet light. Cutter (139) proposed a complex method for determination of selenites, selenate, dimethyl selenide, and dimethyl diselenide in natural waters. In this method, volatile methyl compounds of selenium are washed from a sample by a stream of oxygen. and inorganic forms of selenium are selectively reduced to the hydride and trapped together with selenides in liquid nitrogen. The selenides are separated by gas-liquid chromatography and measured in a quartz tube furnace. The detection limit is of the order of several parts per trillion. The time of analysis was 15 and 30 min/sample for Se (IV) and Se (VI), respectively. Pierce et al. (136) described a rapid automatic method for determination of trace amounts of selenium and arsenic allowing for measurement of 70 samples for 1 hr with a detection limit of 0.011 µg As/l. and 0.019 µg Se/l. and a recovery of 93–107% for As and 96–100.8% for Se.

**Biological Samples.** Paralescu and Tascadanescu (155) reviewed extensively determination of many elements, among them selenium, in biological material by AAS and FAAS. Lund et al. (126), employing electrochemical preconcentration on a filament for estimation of selenium and tellurium by flame AAS obtained detection limits of 5 µg Se/l. and 50 µg Te/l.

Cornil et al. (123) discussed in detail determination of selenium in feedstuffs, fruit, and vegetables (down to 0.1 µg/ml) by AAS.

Ihnat and Westerby (27) used FAAS for estimation of selenium in tissues and powdered milk after mineralization in a HNO3–HClO4 mixture, precipitation of selenium with ascorbic acid and dissolution in a mixture of 0.6N HNO3 and 4.2N HClO4. Then Ihnat reported (24) application of a similar procedure for determination of selenium in the range of and below 1 µg/g in various other materials, including flour and animal tissues with addition of nickel salts (5 mg/ml) into analyzed solutions in order to improve precision of the assay. The detection limit so obtained was 25 ng/g. Neve and Hancoeq (128) determined traces of selenium by FAAS after extraction of mineralized samples with toluene solution of 4-chloro-1,2-diaminobenzene and obtained a detection limit of 10 ng/ml.

Ishizaki (53) employed FAAS for determination of selenium in biological material (down to 0.01 µg/g) after oxygen-flask combustion of samples. So obtained solution was purified on a cation-exchange resin from Cu, Bi, Hg, Ag, and Te ions, extracted with a dithizone solution in CCl4, and the dithizonates formed, together with a Ni(NO3)2 were atomized in a carbon tube.

For determination of selenium in biological material the HGAA was also used thanks to it high
sensitivity and practically negligible matrix effects. Fiorino et al. (38) described a semiautomatic hydride generator for As, Se, Sb, and Te enabling determination of these elements in food. Samples were combusted with HNO₃-H₂SO₄-HClO₄ (4:1:1), added with NaI (as a preliminary reductor of Se (VI) and As (V)) and finally with a NaBH₄-NaOH solution. The selenides were formed directly into air-hydrogen flame. Detection limits were 10–20 μg/g for all the elements (for 1 g sample) with recoveries exceeding 96%. Clinton (25) elaborated a routine method for estimation of selenium in blood and in plants, in the range of 0.01–0.50 μg/g, based on mineralization of 1 g samples with a HNO₃-HClO₄ mixture, hydride generation by controlled addition of NaBH₄, and atomization in the air-hydrogen flame. Ng and McSharry (36) determined selenium in animal-feed premix (0.002–0.4%) by HGAA following combustion of the material in a HClO₄-H₂O₂ mixture. They described a modification of the Varian Model 64 analyzer of As, Se, and Hg enabling application of NaBH₄ instead of the zinc slurry for the reduction.

Vijan and Wood (26) estimated selenium in plants by an automatic method using hydride generation and atomization in a quartz tube. Dried and ground plants (200 g) were heated with a HNO₃-HClO₄ mixture at a temperature of 125°C overnight and added with NaBH₄; the hydride formed was transferred into a quartz tube with a stream of argon. This method enables analysis of 50 samples per day with a detection limit of 25 ng Se/g.

Inhat (36) compared two techniques of selenium estimation in food: HGAA with detection in the argon-hydrogen flame (I) and carbon furnace atomization (II) with addition of Ni²⁺ salts (5 mg/ml) and reported detection limits of 2.5 and 25 ng/l, respectively, for methods I and II. Siemel and Koteel (50) constructed a simple apparatus for optimization of estimation of selenium and arsenic by HGAA. The hydrides formed were frozen out in a U-tube at liquid nitrogen temperature and introduced into the quartz tube atomizer. The authors obtained sensitivities close to theoretical limits: 5.5 × 10⁻⁷ abs. units/g for As and 1.5 × 10⁻⁷ abs. units/g for Se, and applied this method for determination of selenium in food, plants and feedstuffs.

Air and Soil. There are few papers in the literature dealing with estimation of selenium in air (127) and geological materials (123, 140, 141) by AAS. Lavrakas et al. (140) determined selenium in rocks after combustion with a mixture of 40% HF and 16M HNO₃ (1:1). Application of tantalum allowed for a lowering of the detection limit of this method down to 0.06 μg/g as compared with the usual value of 0.1 μg/g. Ohta and Suzuki (141) estimated selenium in rocks by FAAS, with a detection limit of 1.4 × 10⁻¹⁰g.

Apart from absorption techniques, atomic fluorescence methods were also used. Thompson (28) employed the technique of hydride generation and measurement of hydride fluorescence for determination of Se, As, Sb, and Te in feedstuffs and sea water. Sensitivities obtained for all the elements (0.06 ng Se/ml) were much higher (5–30 times) than in the case of AAS.

Gas-Liquid Chromatography (GLC)

Estimation of selenium by GLC is based almost exclusively on measurement of the amount of piazselenol formed in the reaction of Se (IV) with an appropriate reagent in acidic media. Piazselenols are easily extracted with organic solvents (most frequently toluene) in which they can be subsequently determined by spectrophotometric, fluorimetric, or chromatographic methods. In GLC, piazselenols are usually estimated with an electron capture detector (ECD) due to its highest sensitivity and selectivity with respects to these compounds (Table 5). Apart from the superior sensitivity and selectivity, the GLC method allows for elimination of interference from the matrix.

Nakashima and Toei (161) first used the GLC method for estimation of selenium with 4-chloro-o-phenylenediamine, achieving a sensitivity of 4 × 10⁻⁵g. Shimoishi et al. found 1,2-diamino-4-nitrobenzene to be a more sensitive reagent and employed it for determination of selenium in sulfuric acid (162), tellurium (156), sea water (157), plants (45), copper and its salts (163), and milk and its products (44). The same reagent was used for estimation of selenium in copper (164), biological (47, 160) and environmental (160) samples, and estuarine waters (165).

For chromatographic assay of selenium, 2,3-diaminonaphthalene (55), 1,2-diamino-4,5-dichlorobenzene (43), 4-chloro-1,2-diaminobenzenes (156, 166, 167), 4-bromo-1,2-diaminobenzone (166), and N, O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) (168) were also used.

For a further improvement of sensitivity in the determination of selenium, Shimoishi (159) studied 13 different derivatives of 1,2-diaminobenzene and found 1,2-diamino-3,5-dibromobenzene to be most sensitive and enabling for achievement of a detectability level of 1 ng. With the latter reagent, it was possible (158) to estimate directly Se (IV) and total selenium in fresh waters at a level of 2 ng/l by GLC.

Determination of selenium in biological samples by GLC requires previous decomposition of organic
matter, usually performed with HNO₃ (44, 45), HNO₃-H₂SO₄-HClO₄, and Mo (VI) (43) or HNO₃ and Mg (II) (47). Utilization of nitric acid for mineralization prevents ashing and therefore selenium losses but results in disturbing peaks on the chromatograms. These peaks can be due (47) as to products of decomposition of the acid as to products of its reactions with diaminobenzene derivatives. Shimoishi (44) partly solved this problem using a preliminary extraction of mineralized samples before piazselenol formation but this procedure is not always satisfactory (47). Stijve and Cardinale (43) employed purification on Florisil, but this is time-consuming. Poole et al. (47) performed two-step combustion to avoid purification: with HNO₃ and Mg (II) at 80-90°C and then in a muffle furnace at 500°C. GLC enables determination of both Se (IV) and Se (VI) in natural waters (44, 158) and in biological samples (44). The combination of GLC and AAS made possible assay of dimethyl selenide and dimethyl diselenide (142). GLC in conjunction with a microwave emission spectrometric detection system yielded a detection limit of 40 × 10⁻¹² g (with 4-nitrodiaminobenzene) (160). Recently Flinn and Aue (169) proposed a photometric detector for selenium analysis which enables determination of 2 × 10⁻¹² g Se/sec. Buchta et al. (170) proposed a radio-gas chromatographic separation of metal chelates allowing detection of even 10⁻¹⁵ g of the metal.

**Spectrophotometric Methods**

Since Hoste (171) and Hoste and Gillis (172) proposed 3,3'-diaminobenzidine as a sensitive reagent for selenium, many reports appeared offering more sensitive and stable reagents, among them 1,2-diaminobenzene (173) and some of its 4-derivatives (174), 2,3-diaminonaphthalene (175, 176), 1,8-diaminonaphthalene (177), diaminochrysazin (178), thioalicylamide (179), o-hydroxythiobenzhydrazide (180), sodium diethylthiocarbamate (181,182) and 4,5-diamo-6-thiopyrimidine (183). Osburn et al. (184) described a simple method of estimation of selenium in water solutions consisting in oxidation of hydroxylamine hydrochloride to nitrous acid by selenium acid followed by diazotization of sulfanilamide by the produced nitrite and by subsequent coupling of a diazonium salt with N-(1-naphthyl) ethylenediamine dihydrochloride. This method allows for estimation of 0.1 μg Se/ml and interference comes only from Cu (II) and Se (VI) salts which can be removed by ion-exchange [Cu (II)] or heating a sample with 4-5M HCl until boiling [Se (VI)].

Kawashima et al. (185) elaborated a sensitive catalytic method of spectrophotometric determination of selenium based on catalysis by Se (IV) of oxidation of p-hydrasinobenzenesulfonic acid to p-diazobenzenediazonium ion which, after coupling with m-phenylenediamine forms an easily detectable

Table 5. Examples of selenium determination in various materials by gas-liquid chromatography (GLC).

| Materials          | Detection limit | Reagent                      | Reference | Determination conditions                                      |
|--------------------|-----------------|------------------------------|-----------|-------------------------------------------------------------|
| Water solutions    | 4 × 10⁻⁶ g      | 4-Chloro-phenylenediamine    | (156)     | Glass column, 2 m × 4 mm, with 15% SE-30 on 60-80 mesh       |
| Milk and its       | 5 × 10⁻⁶ g      | 1,2-Diamino-4-              | (44)      | Chromosorb W; t = 200°C, V₉₅ = 50 ml/min; ECD detector      |
| Sea water          | 2 × 10⁻⁶ g      | nitrobenezene               |           | Glass column, 1 m × 4 mm with 15% SE-30 on 60-80 mesh       |
| Plants             | 5 × 10⁻⁶ g/g    | 4-Nitro-o-phenylened-       | (45)      | Chromosorb W; t = 200°C, V₉₅ = 27 ml/min; ECD detector      |
| Food, plants,      | 1 × 10⁻⁶ g/g    | ene-diamine                 |           | Glass column 1 m × 4 mm with 15% SE-30 on 60-80 mesh        |
| tissues            |                 |                              |           | Chromosorb W; t = 200°C, V₉₅ = 50 ml/min; ECD detector      |
| Blood, urine,      | 5 × 10⁻¹⁰ g     | 2,3-Diamino-                | (55)      | Stainless column 6 ft × 1.8 in, with 3% SE-30 on Chromosorb |
| river water        |                 | naphtalene                  |           | G, 60-80m mesh; t = 165°C; V₉₅ = 40 ml/min; ECD detector   |
| Plants, tissues    | 1 × 10⁻¹² g     | 1,2-Diamino-4-              | (47)      | Column 1.5 ft × 0.25 in. with OV-225 on Suprasorb/OW-HMDS  |
| River and          | 2 × 10⁻⁹ g      | nitrobenezene               | (158)     | 100-120 mesh; t = 210°C; V₉₅ = 35 ml/min; FID or ECD detector|
| sea water          |                 |                              |           | Glass column 1 m × 4 mm with 15% SE-30 on Chromosorb        |
| Tissues            | 1 × 10⁻⁹ g      | 1,2-Diamino-3,5-            | (159)     | W 60-80 mesh; t = 200°C; V₉₅ = 28 ml/min; ECD detector      |
| Plants, tissues,   | 40 × 10⁻¹² g    | dichlorobenzene              | (160)     | Glass column 1 m × 4 mm with 15% SE-30 on Chromosorb        |
| dust               |                 |                              |           | W 60-80 mesh; t = 200°C; V₉₅ = 28 ml/min; ECD detector      |

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ble orange dye. This method makes possible estimation of 0–2 μg Se/25 ml solution.

Dessai and Paul (181) proposed a simultaneous colorimetric determination of Se (IV) and Se (VI) with sodium diethylthiocarbamate. Examples of spectrophotometric determinations are given in Table 6. Keller and Johnson (187) described a spectrophotometric method of estimation of selenium with 3,3'-diaminobenzidine coupled with isotope dilution for correction of selenium losses. With this method it is possible to estimate several hundred micrograms Se per gram material; it was used for assay of selenium in yeasts.

For determination of selenium in biological material, 3,3'-diaminobenzidine and 2,3-diaminonaphthalene were used most frequently. Application of these reagents was discussed in detail by Broad and Barnard (188), Nazarenko and Ermakov (189), Masson (9), and Taussky et al. (190). 3,3'-Diaminobenzidine requires pH ≥ 5 for quantitative measurements (191) which is inconvenient especially for biological samples subjected to mineralization. Selenium was also determined in biological material with 1,2-diaminobenzene (192, 193) and its 4-chloro (186) and 4-nitro (46) derivatives, which made possible assay in strongly acidic solutions, practically without interference from other metals (46, 174).

Chan and Riley (194) estimated selenium content of sea water by a similar method but with an additional separation of selenium from iron by ion-exchange.

Terada et al. (186) determined selenium (0.3–10 ppm) in rocks, marine sediments, and plankton after converting the element into SeBr4, which was distilled off and assayed colorimetrically as piazselenol.

**Other Methods**

Reaction products of 3,3'-diaminobenzene (DAB) and 2,3-diaminonaphthalene (DAN) with Se (IV) show a strong fluorescence which was utilized for fluorimetric determination of the metal in many materials (195-201). The fluorimetric method is, however, very sensitive to interference from other coextracted compounds. Despite this, it is recommended by EPA (8) for determination of selenium. The method requires isolation of selenium with 3,4-dithiol and employment of EDTA, sodium fluoride, and sodium oxalate as masking agents. It is sensitive and makes possible estimation of selenium in the range of 0.005–100 μg. A critical review of fluorimetric methods of determination of selenium is given by Michie et al. (202).

Waliszewski and Skupin (203) estimated selenium in the range of 0.06–3 mg/kg (0.5–1 g samples), using DAB and toluene extraction. Nazarenko et al. (40) assayed selenium in food with DAN at a sensitivity of 0.001 μg/g. Haddad and Smythe (29) employed DAB and decalin extraction in estimation of selenium in plants mineralized with HNO3-HClO4 mixture. They used EDTA and hydroxylamine hydrochloride for masking. Chan (30) improved the fluorimetric method with DAN by introducing extraction with hexane. Olson et al. (31) proposed a modification of the official method of selenium determination in plants (AOAC 3074), consisting in extension of the combustion time, introduction of more stable reagents, and employment of cyclohexane instead of decalin for extraction. This modified method was applied by Schrauzer and White (204) for estimation of selenium in blood and diet finding a significant correlation between the selenium level in whole blood and that in diet for several countries, among them the U.S., Canada, and Japan. The fluorimetric method was also used by Hiraki et al. (205) for determination of Se (IV) and Se (VI) in sea water (with DAN), by Beal (41) for fish tissues mineralized in HNO3-HClO4-H2SO4, and by Schnepef (206) for rocks (< 0.1 μg Se/g). Brown and Watkinson (207) proposed an automatic method for estimation.

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Table 6. Examples of selenium determination by spectrophotometry.

| Reagent                               | Wavelength, nm | Range of determination or detection limit | References                        | Remarks                          |
|---------------------------------------|----------------|-------------------------------------------|-----------------------------------|----------------------------------|
| 3,3-prime-Diamino-benzidine           | 420            | 0.1–10 μg/ml                              | (171, 172)                        | Toluene extraction, pH 6.7; interference: Au, Br, Cr, Mo, Sn, V, W, Zr, and oxidation agents |
| 2,3-Diaminonaphthalene                | 380            | 0–4.00 μg/ml                              | (176)                             | Toluene extraction, pH 1.5–2.5; interference: Cu, hypochlorite, and reducing agents |
| 1,2-Diaminobenzene                    | 335            | 5–25 μg/ml                                | (173)                             | Toluene extraction, pH 1.5–2.5; interference: Fe (III), Sn (IV), and iodide ions, but Fe (III) can be masked with EDTA |
| 4-Chlorodiaminobenzene                | 341            | 0.3–10 μg/g                               | (186)                             | Toluene extraction at low pH |
| 4-Nitrodiaminobenzene                 | 350            | 3 μg/g                                    | (46)                              | Toluene extraction, pH < 2 |

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of nanogram amounts of selenium and employed it for a direct assay of blood. It is based on a measurement of fluorescence of 4,5-benzopiazelenol in cyclohexane and allows for measurements of 40 samples per hour with a detection limit of 0.44 ng/g.

Selenium was also determined by electrochemical methods using both anodic (32, 208, 209) and cathodic stripping voltammetry (48, 210, 211). Andrew and Johnson (32) reported a procedure for estimation of Se (IV) by anodic stripping voltammetry with a rotating gold disc electrode in mineralized (HNO₃–HClO₄) biological samples. The selenium content was determined from the +0.8 V peak; the detection limit was 0.04 ppb. Dennis et al. (211) determined selenium by cathodic stripping voltammetry with a hanging mercury drop electrode. They separated selenium from contaminations by complexing of other metals and reduction of selenium by NaBH₄ to a hydride absorbed then in an alkaline solution. Graphite electrode was used, too, for estimation of Se(IV) in water solutions (209, 212). Holak (48) in this way assayed selenium in mineralized [HNO₃ and Mg(NO₃)₂] food with a detection limit of 0.1 ppm.

Recently there has been a growing interest in determination of many elements, among them selenium, by x-ray induced fluorescence (XFA). This method makes possible simultaneous estimation of a number of elements, often without a necessity of previous sample preparation. Selenium is determined by measurement of its Kα line (11.2 KeV) with a semiconductor detector (e.g., Si/Li) and computer-coupled multichannel analyzer. By this method selenium was estimated in geological samples and coal fly ash (213), airborne particulates (214) and fresh water (215). Strausz et al. (23) and Holynska and Markowicz (54) used the XFA method for determination of selenium in mineralized biological samples reaching a detection limit of 0.2 μg in a 5-g sample (23).

Apart from the above methods, differential pulse polarography (216), nephelometry with DAN (10–300 ppm) (215), emission spectrometry with a plasma source (218–220) and induced x-ray emission (221) were used, among others, for estimation of selenium. Some examples of selenium determination by above mentioned methods are given in Table 7.

It has been shown that at present numerous methods are available for determination of trace amounts of selenium traces at a subnanogram level. The choice of a particular method will depend on the type of problem studied, accessible equipment and analytical experience of the analyst. If the question consists only of estimation of selenium, the choice can be made, e.g., between fluorimetry, chromatography, or spectrophotometry. In a case of multielemental analysis, the method of choice would be rather neutron activation analysis, atomic absorption spectroscopy, or x-ray fluorescence analysis. It should be emphasized that despite the high costs, neutron activation analysis is the most universal method for determination of elements in a variety of materials. Moreover, it is now possible to do sensitive neutron activation analysis with a relatively low-cost moderate reactor (86, 87).

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