CHAPTER 4

Sample Dissolution Reagents for Beryllium[*‡]

Applications in Occupational and Environmental Hygiene

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Abstract

A variety of sample preparation methods and reagents for beryllium have been used for the dissolution of this element prior to its analytical determination. This chapter provides an overview of methods for beryllium dissolution by

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digestion and extraction techniques for a number of sample media, with emphasis on reagents used to prepare samples of interest in the environmental and occupational hygiene fields. Methods normally target the dissolution of the total amount of beryllium originally present in the collected sample. Sample matrices of interest include aerosols, surface samples, ores, soils, beryllium metal, beryllium oxide (including high-fired BeO), and beryllium alloys. Samples of concern for occupational health monitoring include primarily those collected from workplace air and from surfaces. Attributes of the various reagents and techniques are discussed.

4.1 Introduction

In this chapter, sample preparation reagents and dissolution procedures for beryllium are considered, with emphasis on environmental and occupational hygiene samples. There is a wealth of knowledge on sample preparation techniques for subsequent determination of beryllium in a variety of environmental matrices such as airborne particles, soils, sediments, and the like. Unfortunately, much of what is known about sample preparation methods for beryllium in environmental media appears in the older (pre-1980) literature and is often missed by modern-day computer literature searches. In an effort to ameliorate these problems related to the limitations of computerized databases, this chapter strives to provide an overview of some of the important yet "forgotten" literature, while also giving updated information from more recent relevant studies in the subject area. It is not the intention here to exhaustively recount information that has been previously published, but rather to provide a brief survey of the historical literature, along with an update citing more recent investigations in the realm of study.

4.2 Background

In order to measure the beryllium content in samples collected from workplace air, from surfaces in occupational settings and/or other matrices, it is normally necessary to dissolve the collected sample prior to subsequent instrumental measurement of beryllium. Through dissolution, beryllium is ionized and is present in solution as the dication. Techniques to perform this dissolution have historically required acid digestion, many of which have evolved from dissolution procedures for ores, soils, sediments, and other geological sources of beryllium. With these issues in mind, this chapter begins with an overview of sample dissolution procedures for bulk samples, with later discourses on methods for preparing beryllium samples for industrial hygiene monitoring purposes (*e.g.* air, wipe and vacuum samples).

4.3 Beryllium in Geological Media

An overview of the sample preparation methods for geological matrices such as ores and soils is a relevant starting place for discussions of beryllium determinations in environmental media. Dissolution of rock and soil samples is a challenging and often difficult task and, over the years, techniques to decompose and solubilize such media for subsequent determination of beryllium have been investigated and optimized.

4.3.1 Beryllium Ores

Decomposition of beryllium-containing ores such as beryl and bertrandite is ordinarily carried out by means of a fusion process.[1,2] Extremely high-temperature fusion techniques are useful for dissolving refractory materials such as silicates, which are present in high concentration in ores and most other bulk geological media. Sodium carbonate–sodium tetraborate[3–5] and potassium fluoride–sodium pyrophosphate[1] fusions have been shown to quantitatively dissolve beryllium in ores, but treatments with nitric acid alone give low beryllium recoveries from ore samples. Similar fluoride-assisted fusions have been reported for the breakdown of beryl ores and intermediate metallurgical products therefrom.[6–8] Overall, fusion procedures are tedious, time-consuming, and require great skill and extensive experience. Moreover, to complete the dissolution process, it is necessary to carry out subsequent dissolution steps with strong acids such as sulfuric, boric and perchloric acid after the fusion itself is first carried out.

Hydrofluoric acid aids greatly in the dissolution of silicates and is often used in the decomposition of fused ores and other geological specimens. For instance, aqua regia/HF microwave digestion as a first step in the sample preparation process has become routine for the dissolution of beryl.[9] Many of the techniques employing HF that have been found to function well for the breakdown and dissolution of beryllium-containing ores have also been employed for sample preparation purposes on other media of environmental and occupational hygiene interest.

4.3.2 Soils and Silicates

Like ores, soils contain large amounts of silicates (often 50% by weight or greater), and the decomposition of such samples for subsequent beryllium determination requires that these refractory compounds are completely dissolved. This is because the beryllium present is often bound up in the silicate material itself. Hotplate, microwave and similar high-temperature digestions utilizing acid mixtures that include hydrofluoric acid have historically been used for the dissolution of soil samples and related silicate-containing media such as sediments and sludges. High-temperature digestions using mixtures of acids (usually nitric acid plus hydrochloric, perchloric or sulfuric acids, with addition of hydrofluoric acid to facilitate the dissolution of silicates) are commonly used for the dissolution of soils and related samples for subsequent beryllium determination.[10–13]

Because skin exposures in the laboratory, particularly to HF, are extremely dangerous, it is desirable to investigate alternative reagents that may

Table 4.1 Dissolution techniques for beryllium in geological samples.

Matrix(es)	*Dissolution Method/Reagents*	*Reference*[a]
Beryl, bertrandite and other ores	(1) $Na_2CO_3/Na_2B_4O_7$ fusion, >900 °C (2) $HCl/HClO_4$ hotplate digestion	1
Beryl, bertrandite and other ores	(1) $HF/KF/Na_4P_2O_7$ fusion (2) $H_2SO_4/Na_2SO_4/HCl$ digestion	1,4
Ore samples	(1) $Na_2CO_3/Na_2B_4O_7$ fusion, 1000 °C (2) HCl/H_2SO_4 (+ $HNO_3/NaOH/H_2O_2$, if necessary) digestion	3
Beryl and bertrandite ore samples	(1) $Na_2CO_3/Na_2B_4O_7$ fusion (2) HCl/alcohol hotplate digestion	5
Beryl ores	(1) NaF/Na_2CO_3 fusion, 1400 °C (2) NH_4HF_2 treatment (1000 °C)	8
Beryl ores	$HF/HNO_3/HCl/H_3BO_3$ closed-vessel microwave digestion	9
Beryl ores	(1) NaF fusion, 900 °C (2) H_2SO_4/HNO_3 digestion	9
Rock (terrestrial, meteorites and lunar samples)	(1) NaF/Na_2CO_3 fusion (2) HCl dissolution	10
Soils	$HNO_3/HF/HClO_4$ hotplate digestion	11,12
Sediments	HF/H_2SO_4 hotplate digestion	13
Soils and silicate materials	(1) KHF_2/Na_2SO_4 fusion, ~800 °C (2) $HClO_4$ (or H_2SO_4) dissolution	14

[a] Details on the various sample preparation procedures can be found in these references.

nonetheless be effective for dissolving silicate materials. Hence, other less hazardous sample preparation methods for soils and related materials have been attempted in which the use of HF was avoided. As an example, an alternative but effective means for decomposition of soil samples entails fusion with a mixture of KHF_2 and Na_2SO_4.[14] This procedure was used as a first step in the separation of ^{10}Be from soil and silicate samples. Additionally, ammonium bifluoride (NH_4HF_2) has been shown to be useful for the dissolution of quartz silicate materials,[15] and is also effective in solubilizing beryllium subsequent to fluoride fusions of bulk samples.[6,8] Also, the utility of NH_4HF_2 for solubilizing beryllium oxide,[16] beryllium hydroxide[16,17] and metallic beryllium[17] has been reported in relevant texts.

Table 4.1 summarizes some of the representative sample preparation procedures used for the dissolution of beryllium in geological samples such as ores and soils. As can be seen from the table, a number of different protocols have been employed and shown to be effective.

4.4 Occupational Hygiene Samples

Of principal concern for the purposes of this overview is the dissolution of beryllium from samples of interest in the occupational hygiene field, with a focus on specimens collected from workplace air and surfaces. In the United States, the most conservative regulatory occupational exposure levels (OELs) for beryllium in air and on surfaces have been established by the US Department of Energy (DOE).[18] Hence for compliance purposes, especially within the DOE complex, it is usually air filters and wipe samples which must be analyzed for beryllium content. This ordinarily requires dissolution of the collected particulate matter plus the sampling medium (*i.e.* the filter or wipe material) using acid digestions. HF is often employed in digestions for dissolving refractory materials such as silicates and beryllium oxide calcined at temperatures in excess of 1500 °C ("high-fired" BeO). More recent work has shown, however, that beryllium extractions with ammonium bifluoride can be successfully performed even from challenging samples, but without dissolving the sampling media (*e.g.* filters or wipes). Methods used to prepare air filters, wipes, and related samples prior to beryllium determination are discussed below.

4.4.1 Workplace Air Samples

Occupational air monitoring of workers potentially exposed to airborne beryllium particles began in earnest in the mid 20th century due to the recognition of this element as a highly toxic workplace hazard.[19] Collection of beryllium aerosols using impingers and air filter samplers have been described.[1,2] Latterly the use of filters for the capture of airborne beryllium, especially those comprised of mixed cellulose ester (MCE), has become the industrial hygiene sampling method of choice for this element.

As to sample preparation methods, early reports described hotplate digestion of cellulosic air filter samples in (primarily) mixtures of nitric and sulfuric acids prior to spectrographic measurement of extracted beryllium.[20,21] Digestion procedures utilizing nitric along with hydrochloric[2] and perchloric[22,23] acids for the dissolution of air filter samples for subsequent beryllium determination were published in later years. A standardized analytical method based on the use of nitric and sulfuric acids (with perchloric acid as an option) for sample preparation was promulgated by the American Industrial Hygiene Association (AIHA) four decades ago.[24] Later, a "tentative" method describing nitric/sulfuric acid digestion for cellulosic filters, and nitric/hydrochloric acid digestion for glass-fiber filters, was published.[25] A related sample preparation method for airborne beryllium collected from emission sources, which relies largely on perchloric acid as a hotplate digestion reagent, was published[26] and field-tested through an interlaboratory trial.[27] Nitric/sulfuric acid digestions are also routinely used for preparation of ambient air and other environmental samples.[28] As hotplate digestion procedures for subsequent beryllium determination, these sample preparation methods are still in wide use to this day.[29]

"Dry ashing" methods, in which quartz-fiber filters,[23] cellulose filters,[29–32] and paper tape[31] samples are ignited at high temperature (500–700 °C) prior to dissolution of the remaining ash in acid, have also been described in earlier papers. These sample preparation procedures, which were originally suitable for colorimetric, fluorimetric or spectrographic analysis, were later applied prior to beryllium measurement by atomic emission spectrometric analysis.[33] They are infrequently used because dry ashing techniques often entail hazardous protocols that can be difficult to carry out and may not be necessary for air sample preparation purposes.

Digestion methods in which HF is employed for dissolution of difficult aerosol matrices, notably refractories such as high-fired BeO, have been reported.[34,35] Because HF is particularly suitable for the dissolution of silicate materials, this acid is used in a French method for dissolving samples collected on quartz-fiber filters.[36]

Leaching of air filter samples with dilute sulfuric acid has been explored for the dissolution of beryllium.[37,38] The procedure is applicable to more soluble beryllium compounds, but is not recommended for insolubles such as refractory beryllium compounds. In a noteworthy application, a sample preparation procedure was proposed in which air filter samples were subjected to boiling in a dilute nitric acid–potassium bisulfate mixture.[39] This method was shown to be effective for dissolving beryllium, including beryllium oxide, in particles over a size range of 1–150 μm.

A sequential extraction procedure for beryllium in air, in which an effort was made to speciate beryllium compounds based on their relative solubilities in chemical reagents of varying strength, has been proposed.[40] The protocol is outlined as follows:

(1) Soluble beryllium salts are dissolved by means of a brief ultrasound treatment in 0.01 M HCl.
(2) Be(II) from metal is then extracted by sonication in 0.1 M copper sulfate.
(3) Be(II) ascribed to BeO is subsequently dissolved by hotplate digestion in a mixture of concentrated nitric and sulfuric acids.
(4) Siliceous Be(II) is dissolved by subjecting the remaining undissolved residue to hotplate digestion in a solution of concentrated nitric and hydrofluoric acids.

Interest in sequential extraction stems from the notion that different metal compounds in air can demonstrate varying toxicities.[41] Further work is required in order to make sequential extraction methods more rugged, and thereby ensure comparability of results obtained from different laboratories.

There are a number of standardized methods for the preparation of airborne beryllium samples collected from workplace atmospheres, and these have been summarized in recent papers.[42,43] An overview of the procedures published by both governmental agencies and consensus standards organizations was provided in these reviews. At the same time, an extensive survey of laboratories performing beryllium-in-air analyses was carried out.[44] Despite the existence of readily available harmonized procedures, it was found that there was little conformity in the reagents which the surveyed laboratories used to prepare air filter samples for subsequent beryllium determination.

Table 4.2 Standardized dissolution techniques for beryllium in workplace air filter samples.

Method	*Dissolution Procedure/Reagents*	*Reference*
NIOSH 7102	HNO_3/H_2SO_4 hotplate digestion	45
NIOSH 7300	$HNO_3/HClO_4$ hotplate or microwave digestion	45
NIOSH 7303	HNO_3/HCl hot block digestion	45
NIOSH 7704	NH_4HF_2 extraction	45
OSHA ID-125G	$HNO_3/HCl/H_2SO_4$ hotplate digestion	46
OSHA ID-206	HNO_3/HCl hotplate digestion	46
HSE MDHS 29/2	HNO_3/H_2SO_4 hotplate digestion	47
INRS Fiche 003	HNO_3/HF ultrasonic extraction	36
ASTM D7035	Options for various acid mixtures; hotplate or microwave digestion	48
ASTM D7202	NH_4HF_2 extraction	51
ASTM D7439	Options for various acid mixtures; hotplate, hot block, or microwave digestion	50
ISO 15202-2	Options for various acid mixtures; hotplate digestion, microwave digestion or ultrasonic extraction	49

Table 4.2 presents a summary of the salient standardized methods used widely at the present time, along with information about dissolution reagents recommended, for preparing workplace air samples for subsequent beryllium measurement.[36,45–51] The methods listed are applicable to occupational air samples collected using inhalable, thoracic, or respirable samplers.[52] Procedures that utilize nitric and/or hydrochloric acids are applicable to the dissolution of beryllium compounds that are more highly soluble.[53] However, methods that rely on sulfuric or perchloric acids are required for quantitative beryllium recovery from refractory matrices such as high-fired beryllium oxide.[54] Dilute ammonium bifluoride has also been shown to be effective for dissolving beryllium in air filter samples, including samples containing BeO calcined at high temperatures.[55–57] Dissolution of silicious material in airborne particulate samples requires the use of HF[36] or ammonium bifluoride.[15]

4.4.2 Surface Samples

Beryllium in surface dust is usually collected using wipe sampling techniques,[42,58] but vacuum sampling methods are important for dust collection from non-smooth substrates.[42,59] Cellulosic or polyvinyl alcohol wipe materials are recommended for sampling of beryllium in surface dust, and a consensus standard wipe sampling method has been published.[60] For collection of surface dust from rough or porous surfaces, a consensus standard micro-vacuum sampling technique has been promulgated.[61] Compared with air filter samples, samples of surface dust ordinarily contain much more collected material, as

Table 4.3 Standardized dissolution techniques for beryllium in surface samples.[a]

Method	*Dissolution Procedure/Reagents*	*Reference*
NIOSH 9102	$HNO_3/HClO_4$ hotplate or microwave digestion	45
NIOSH 9110	NH_4HF_2 extraction	45
OSHA ID-125G	$HNO_3/HCl/H_2SO_4$ hotplate digestion	46
OSHA ID-206	HNO_3/HCl hotplate digestion	46
ASTM D7202	NH_4HF_2 extraction	51

[a] The methods listed are normally applicable to wipe samples, but can also be modified for vacuum and bulk samples collected from surfaces.

well as greater masses of sampling media. Treatment of these materials for sample preparation purposes generally requires greater volumes of acid solution compared with airborne particulate material collected onto air filters.

In a report from over four decades ago,[2] settled dust samples were first treated with nitric acid to destroy any organic material present; sample decomposition was then completed using a potassium fluoride–sodium pyrosulfate fusion. An alternative technique described in an early paper[30] called for (1) dry ashing at 800 °C to destroy carbonaceous material, followed by (2) fusion at 600 °C using potassium bisulfate to ensure complete dissolution of calcined beryllium oxide.

At present, most industrial hygiene laboratories avoid the use of fusion and dry ashing methods for preparing surface dust samples for beryllium analysis, and instead rely mainly on strong acid digestion techniques.[43,44,53] Alternative procedures for preparation of wipe samples, such as boiling in a mixture of dilute nitric acid and potassium bisulfate,[39] or extraction in dilute aqueous ammonium bifluoride,[55–57] have also been proposed. The latter methodology has been standardized and published in the form of an international voluntary consensus standard[51] and also as an approved National Institute for Occupational Safety and Health (NIOSH) analytical method.[45]

A list of standardized methods for preparing samples of surface dust for subsequent determination of beryllium is presented in Table 4.3.[45,46,51]

4.4.3 Bulk Samples

Frequently there is a need to prepare bulk samples for subsequent determination of beryllium. Apart from airborne and surface dust samples, the importance of analyzing soils and accumulated settled dust for beryllium content has arisen at several DOE sites and other locations where nearby soils may have been contaminated with beryllium and/or beryllium compounds. On a number of the DOE sites, there are buildings which may have been used for beryllium work in the past and have been vacant for decades. Such locations are known within DOE as "legacy" sites. In many of the buildings on legacy sites, thick layers of dust with unknown levels of beryllium contamination have built up over the years. To investigate the possibility of environmental sources of beryllium, there is interest in testing samples of the dust from these buildings. These accumulated dust samples can be collected by bulk sampling methods and then analyzed.

The decomposition methods for bulk environmental samples are generally similar to those described above for geological samples such as soil and rock (Table 4.1). In such cases, it is ordinarily necessary to employ a hotplate or microwave digestion technique which uses HF in the acid mix.[62–65] Of course, the aforementioned fusion methods for ore and soil samples may also be applicable. However, fusions must be carried out carefully, for (among other considerations) it is possible that losses of volatile beryllium compounds may occur, for example in samples containing organic material.[66] "Direct" analysis of some matrices can be carried out by spectrometric methods,[67] although a dry ashing procedure may be necessary prior to analysis.[68] In other work, a novel autoclave decomposition technique using xenon tetrafluoride, prior to a sulfuric acid extraction, reportedly gave good recoveries of beryllium from coal and ash samples.[69]

Techniques for decomposing bulk samples such as metals, alloys, and ceramics must be sufficiently robust so as to completely dissolve all of the beryllium present. Again, digestion procedures employing mixtures of nitric and hydrofluoric acids have been demonstrated to be effective for dissolving such challenging sample matrices.[70,71] Nevertheless, alternative dissolution methods have been reported, including the use of concentrated phosphoric acid,[72] ammonium bifluoride,[17,56,57,73] or fluoride fusions.[7,17]

4.5 Summary

The determination of beryllium in samples of interest in the occupational and environmental hygiene arena ordinarily requires that this element is put into solution prior to its analytical measurement. Alternative "direct analysis" techniques have appeared but, generally speaking, dissolution of the sample matrix is necessary to ensure maximal performance with minimal overall analytical uncertainty. A wealth of information on decomposition techniques for subsequent determination of beryllium was published in the latter half of the 20th century, and the knowledge generated has enabled the promulgation of standardized methodologies. Also, newer extraction techniques that are less hazardous than traditional decomposition methods have been shown to be effective for dissolving refractory beryllium samples.

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