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Experimental simulation of trace element evolution from the excluded mineral fraction during coal combustion using GFAAS and TGA–DSC

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HIGHLIGHTS

- GFAAS profiles provide insights into trace element speciation during coal combustion.
- TGA–DSC complements GFAAS in providing information on trace element vaporization.
- Excluded minerals in coal can be modeled by using metal oxide coated GFAAS furnaces.
- As atomization in not influenced by carbon whereas the Sb and Se atomization do.
- Iron and calcium influence the As and Se partitioning in different ways.

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ABSTRACT

A combination of graphite furnace atomic absorption spectrometry (GFAAS) and thermogravimetric analysis–differential scanning calorimetry (TGA–DSC) was used to simulate the gas–melt partitioning of semi-volatile trace elements (TEs), such as As, Sb and Se, from excluded minerals during the initial dynamic step of coal combustion. To properly simulate an exclusion, the effect of carbon in the graphite furnace tubes on TE vaporization was minimized by coating the tube with an inert metal oxide (either ZrO_2 or WO_3). The Arrhenius activation energies of TE volatilization/atomization obtained upon fast heating in such a carbon-free GFAAS microenvironment, with and without mineral matrices, were compared with those obtained in uncoated tubes to verify that the influence of carbon had been eliminated and to obtain insights on the mechanism of TE evolution. Cationic inorganic matrices, such as calcium and iron, influenced the carbon-free evolution of Se and Sb in a different way than in the presence of carbon thus indicating that TE partitioning from mineral exclusions during coal combustion may be significantly different from TE partitioning from organically associated material and mineral inclusions. Calcium increases the Se (and, to some extent, As) retention in the solid phase due to common acid–base chemistry, whereas iron, as well as anionic matrices, such as aluminate and silicate, do not influence TE atomization in mineral exclusions. By contrast, in inclusions these minerals decrease the extent of TE atomization by shielding it from the reducing action of carbon. A significant chemical reduction of As to its elemental form was observed, which does not appear to be influenced by the presence of carbon. By contrast, the extent of Sb and Se atomization depends on this factor, which is different in exclusions compared to inclusions. Thus, the presented method provides information that can be used to predict the predominant TE speciation in the gas phase.

1. Introduction

Trace elements (TEs) such as arsenic, selenium and antimony, are present in coal and released into the environment upon combustion. Many TE species are classified as toxic air pollutants per the U.S. Clean Air Act Amendments (CAAAs) of 1990 [1]. Understanding TE transformations and speciation during coal combustion may help in the determination of their environmental fate and the development of effective mitigation strategies [2–11]. The environmental fate of TEs, to a large extent, is determined by their solid/gas phase partitioning in the combustion system, which

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in turn depends on the TE's form of occurrence in the coal and the influence of coal type on the combustion environment experienced by the TE [1,12].

TEs in coal can be organically associated, occur in mineral inclusions, or present in excluded minerals [13,14]. In each of these regimes, TEs experience a different environment that affects their partitioning. Organically associated TEs are released into the vapor phase due to bond cleavage during carbon oxidation and the very high temperature microenvironment is strongly reducing. Inclusions are surrounded by burning carbon. The mineral matrix softens and partially or completely melts, allowing volatile and semi-volatile TEs to vaporize. By contrast, excluded minerals are less intimately exposed to the effects of carbon oxidation since they reside outside of the individual coal particles. Compared to the organically associated and mineral inclusion fractions, excluded minerals are exposed to lower temperatures and a more neutral/oxidizing environment due to their significant effective distance from the burning coal matrix (carbon) [15–18]. Under neutral/oxidizing conditions, most exclusions are expected to "soften" and rearrange into spherical particles while the most volatile material vaporizes. Expansion can lead to hollow cenospheres which can subsequently crack or shed into smaller material [19]. TEs within the matrix must diffuse to its surface to vaporize [20].

Unfortunately, these different forms of occurrence are not addressed by existing experimental methods [8,21]. Yet simulation of the dynamic partitioning of TEs separately for all three forms of occurrence is essential for accurate modeling. The TGA or flow pyrometer-based methods commonly used for coal combustion kinetic measurements [22–25] provide only the bulk values of Arrhenius activation energies (E_a) related to the thermal release of matter and cannot be used for the characterization of TE evolution since these TEs comprise only a minor fraction of the coal that is either combusted or evaporated (under anaerobic conditions). To our best knowledge, no TE-specific E_a values pertaining to coal combustion have been reported except for one study of pure antimony oxide [26], which evaporates in a completely different chemical microenvironment.

In our previous work, we presented a new method that simulates and measures the partitioning of *organically associated* TEs. This method is based on the use of a completely different carbon-based experimental platform, i.e., a modified graphite furnace atomic absorption spectrometer (GFAAS) [27] to measure kinetic parameters such as TE- and microenvironment-specific E_a values. The method provides a dynamic (fast heating), temperature-programmed evolution under anaerobic conditions with an accurate, *in situ*, detection of only atomic species. Based on these parameters, information about TE behavior during the initial stages of combustion can be obtained at the molecular level of resolution. We also extended the method to simulate the partitioning of TEs present as *mineral inclusions* by introducing homogeneously mixed TE solutions and matrix solutions inside the furnace. These matrices, e.g., silicates, aluminate, calcium and iron, are representative of the major inorganic constituents present in the coal [28].

Next, we extended this method to simulate TE evolution from mineral exclusions by isolating the TEs in the graphite tube from the tube's carbon. This was accomplished by lining the tubes with a high melting point, inert metal (Ta). Several TE-specific E_a values were obtained [29]. However, as was shown in our prior work, despite its attractiveness, e.g., the inherently inert nature of metal covers, metal linings have one significant drawback, namely that only a portion of the graphite surface can be covered [29]. As demonstrated below, metal linings cannot be used as a single method to simulate exclusions.

To overcome the limitations of metal linings, an alternate isolation method has been employed, namely, the use of metal oxide-coated graphite tubes. We postulated that such coatings could be used to more completely isolate the simulated exclusion from the graphite in the furnace tube and thus allow for the creation of a truly neutral environment for TE atomization. A primary goal of this paper is to document the success of this improved method for simulating TE evolution from mineral exclusions. Parenthetically, the role of elemental carbon in TE atomization and vaporization from coal was also assessed in the course of this work. Furthermore, qualitative information on the most likely predominant speciation for each TE in the gas phase was obtained as a function not only of carbon accessibility but also of the mineral microenvironment surrounding the targeted initial TE species.

The use of coatings in GFAAS graphite furnace tubes was reported earlier for the quantitative analysis of elements such as V, Cr, Mo, and Sn to prevent reaction with the graphite and subsequent carbide formation, which decreases the sensitivity of measurements [30–32]. The novel use of such coatings in the current study was to suppress the effect of graphite on TE vaporization/atomization via its chemical reaction with their oxides (reduction).

The use of the following salts as coatings has been reported: $ZrO(AcO)_2$, $ZrOCl_2$, $Zr(NO_3)_2$, Na_2WO_4, NH_4VO_3, $KMoCl_6$, $TiCl_3$, TaF_7^{2-} [30–35], with zirconium(IV)- and tungsten(VI) oxide-based coatings being the most commonly used. Coatings can be formed by two methods: injection [33,34] or impregnation [30–32,34]. Injection consists of repeated introduction of a highly concentrated salt solution inside a graphite tube alternated with subsequent heating cycles [33,34]. Impregnation consists of soaking a graphite tube in highly concentrated salt solutions in a closed vessel under reduced pressure followed by drying [30–32,34]. Since coatings obtained by both injection and impregnation were shown to exhibit similar features [34], injection was chosen for all experiments conducted in this work. This method was preferred because it does not alter the physical properties of the graphite furnace (e.g., conductivity).

The other novel feature of this study is the use of thermogravimetric analysis and differential scanning calorimetry (TGA–DSC) to evaluate the effect of carbon on TE evaporation. Tomeczek et al. showed that the mass loss of major inorganic constituents during coal combustion can be simulated as a mixture of individual minerals in TGA–DSC [13]. However, the instrument limitation of TGA–DSC is in its narrow temperature range, under 1500–1600 °C. Perhaps, an even more important limitation is that the thermal release of minor TE impurities under anaerobic conditions occurs slowly (apparently being thermodynamically controlled), i.e., at lower temperatures than during coal combustion. Due to these limitations, TGA–DSC cannot be used to directly simulate the behavior of TEs during coal combustion in high temperature environments. Yet the method may serve as an important complementary method.

Using a TGA–DSC instrument allows direct measure of TE oxide volatilization, with or without concomitant reduction. Thus the information obtained by this method enhances the mechanistic study of TE evolution. GFAAS activation energies can only provide information about the rate-limiting step of the multistep atomization process because GFAAS exclusively detects atomic species. When TE volatilization activation energies and thermodynamic enthalpy values obtained by TGA–DSC match those obtained in GFAAS, oxide vaporization is confirmed as the rate-limiting step. By contrast, if the low-temperature steps are not rate-limiting for TE atomization, the TGA–DSC values may be lower than the GFAAS values, suggesting that the actual atomization, i.e., chemical decomposition reaction, may be the rate-limiting step for the entire atom evolution process.

In addition, TGA–DSC can be used to assess the reduction potential of the system studied by including activated carbon in select runs. If carbon consistently reduces the effective E_a in both TGA and GFAAS, then carbon-associated chemical reduction reactions