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Review Article

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Pyrohydrolysis, a clean separation method for separating non-metals directly from solid matrix

Abstract

Pyrohydrolysis is a sample preparation technique widely employed for the separation of fluorine, chlorine, bromine, iodine, boron and sulphur from solid samples which include refractive materials that are difficult to dissolve. There is a growing interest in the application of this technique to samples of diverse nature. Pyrohydrolysis is based on the principle that pulverization of a soild sample due to the combined action of heat and steam at high temperature produces volatile compounds of the analytes which are trapped in an alkaline solution for subsequent analysis. Studies reported in the recent past have investigated the effect of various pyrohydrolysis conditions required to pulverise the matrix as well as to convert the analytes into their volatile oxides. Hence, the physico-chemical investigation on one type of the sample is different from the other and such information is very useful while dealing with a new material for its pyrohydrolysis. This mini review is an attempt to highlight a few pyrohydrolytic separations which have significant importance.

Keywords: physico-chemical investigation, soild sample, pyrohydrolysis, thermodynamic principle, non-metals, carrier gas, halogens, sulphur, volatile compounds, fluorine, high temperature, instrumental analysis, separation technique

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Introduction

Pyrohydrolysis (PH) is a separation technique and it is in practice prior to 1950.[1] It is also known as "High temperature hydrolysis". Warf and co-workers utilised this technique for analytical purpose for the first time in 1954.[2] Since then pyrohydrolysis has been widely used for separating halogens, boron and sulphur in solid matrices especially in rocks, minerals, coals, fuels and in many biotic as well as abiotic compounds. The technique is based on the formation of volatile compounds of halogens and other non-metals due to the hydrolysis of halogens and other non-metals at high temperature. Subsequently the volatile compounds can be condensed and collected after driving out them by passing a moist carrier gas. The release of halogens is based on the following thermodynamic principle.

$$MF_{2n} + nH_2O \leftrightarrow MO_n + 2nHF$$

The above reaction is feasible only when the temperature is in the range of 900-1200 °C in presence of water. In practice, the solid sample taken in a quartz or silica boat is heated in a silica or quartz make reaction tube placed in a tubular furnace where a continuous flow of moist carrier gas is maintained. The carrier gas may be either air or oxygen or argon. During this process, the halides are converted into their oxides and subsequently they are converted into their respective acids. For instance, fluorine and boron are converted into HF and H_3BO_3, respectively. Depending upon the nature of the matrix the kinetics of pyrohydrolysis process varies. In order to improve the kinetics of pyrohydrolysis accelerators or catalysts or fluxes are mixed with the samples having slow kinetics. The commonly known accelerators or catalysts or fluxes are U_3O_8[3,4] V_2O_5[5] WO_3[6] and SiO_2[7] and in such case the sample to accelerator mass ratio is required to be optimised to achieve the complete recovery of analytes within the acceptable time of pyrohydrolysis. The volatile acids are condensed and trapped in a dilute alkaline trapping solution, which is more often a dilute solution of NaOH or Na_2CO_3. The sample solution obtained finally in the process is known as pyrohydrolysis distillate, which is free from matrix as well as contaminants. It is considered to be a clean separation as it provides a sample solution which is almost free from reagents. Pyrohydrolysis is unique owing to its capability of separating the analytes directly from the solid samples without carrying out dissolution.

Considering the advantages of pyrohydrolysis it has been used routinely for the separation of halides and boron from diverse matrices.[8–11] Depending upon the concentration of analytes in the pyrohydrolysis distillate several analytical techniques are being employed for the determination of halides and boron. In the last ten years more than 100 research papers have been reported wherein pyrohydrolysis was employed for preparing samples that are amenable to instrumental analysis. Although pyrohydrolysis is one of the simple separation techniques, its application in several fields needed to be explored in addition to the routine applications. Recently, for the first time the separation of molybdenum from uranium matrix by pyrohydrolysis was reported. Therefore, this brief review deals with some of the important applications of pyrohydrolysis reported in the recent past.

Apparatus

Since then the implementation of pyrohydrolysis for analytical purposes, the basic design of the pyrohydrolysis apparatus has not seen significant changes, however, few modifications were incorporated. The common design of the apparatus is simple and it consists of a quartz reaction tube connected at one end to an inlet for moist carrier gas and at the other end is connected to a condenser. The moist carrier gas is produced by passing a suitable gas through boiling water. Figure 1 shows a schematic diagram of a conventional pyrohydrolysis apparatus used for nuclear fuels. The apparatus has a provision to disconnect the carrier gas flow while loading the samples. For the safe handling of radioactive materials as well as for the sake of easy operations, the pyrohydrolysis apparatus was suitably modified

(Figure 2). This modified apparatus consists of an inner reaction tube covered with an outer reaction tube and this arrangement makes the operation ease.

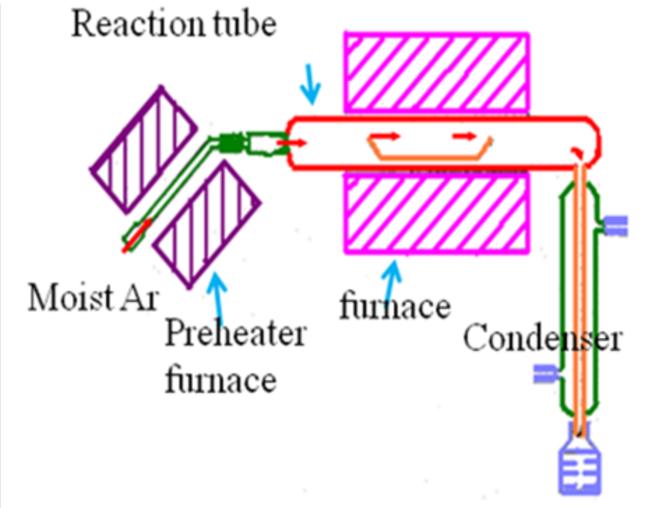

Figure 1 Schematic diagram of a conventional pyrohydrolysis apparatus used for nuclear fuels.

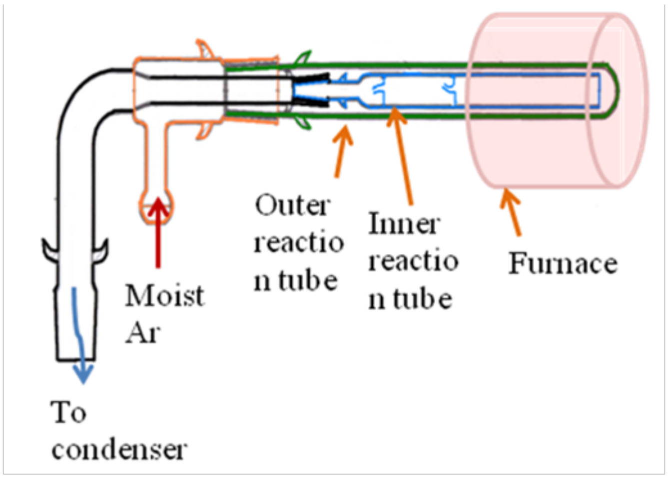

Figure 2 Schematic diagram of a modified pyrohydrolysis apparatus used for nuclear fuels.

Geochemical samples

Several analytical problems related to determination of halides, boron and sulphur in varieties of sample matrices were resolved through pyrohydrolysis method of sample preparation. Remarkable studies have been reported in halide analysis especially in coal, crude oil, nuclear materials, biological materials, geo-matrices and in minerals. Kenji S and co-workers studied the presence of fluorine, chlorine and sulphur in volcanic silicate glasses by carrying out pyrohydrolysis separation followed by their determination by ion chromatography. The crushed silicate glasses were mixed with V_2O_5 and pyrohydrolysed at 1250 °C for 30 minutes.[12] M. Bonifacie et al. described the optimisation of chlorine extraction from silicate rocks of various mineralogy by pyrohydrolysis prior to the precise determination of Cl stable –isotope compositions by gas source, dual inlet Isotope Ratio Mass Spectrometry (IRMS).[13] The study reported an overall Cl extraction yield of 100±8%. Another study by Bernal et al. where the pyrohydrolytic extraction of chlorine from scapolite mineral was employed with a view to determine the stable isotopic composition of Cl employing isotope ratio mass spectrometry (IRMS).[14] Pyrohydrolysis is unique in separating halogens from the soil matrices. In many cases, pyrohydrolysis is employed as a standard technique for comparing the recoveries obtained from other methods or for carrying out analytical validation while establishing a new methodology for halogen separation and determination. Pereira et al. proposed a microwave based volatilisation technique for separating halogens from soil samples wherein pyrohydrolytic extraction of halides was employed with a view to validate the proposed method.[15]

Pyrohydrolysis has been used in analysing large number of geological reference materials. S. Sekimoto and M. Ebihara determined halogens (Cl, Br and I) by radiochemical neutron activation analysis (RNAA) and they also carried out pyrohydrolytic separation to investigate the inconsistencies observed between the RNAA results and literature values. They reported about the incomplete recovery of chlorine in pyrohydrolysis[16] reported a fast and efficient pyrohydrolysis extraction method for iodine from different types of geochemical samples which include internal reference standards of soils, reference materials of bauxite, granite, tonalite, seyenite and feldspars. They investigated the effect of various fluxes such as $PbCrO_4$/PbO, WO_3/$V_2O_5$and V_2O_5 on the pyrohydrolytic decomposition of geomaterials taken for investigation and they found that V_2O_5 is preferred among them as it provided better recovery of iodine while pyrohydrolysing the samples for about 15 minutes at 1060 ºC.[17] Determination of chlorine and bromine in sedimentary and igneous rocks by alkaline fusion followed by ion chromatography detection was proposed by PA Blackwell et al. The results for chlorine were validated by comparing the values obtained from pyrohydrolysis- flow injection analysis.[18] L Pagea et al.[19] studied the halogen behaviour in subducting slaps and for which the halogens viz. F, Cl, Br and I were separated from the samples by pyrohydrolysis. The work provided the complete details of pyrohydrolysis.[19] Fluorine content of several materials was determined using pyrohydrolysis extraction of fluorine and fluoride ion-selective electrode method to determine the sources of F and the pathways of causing fluorosis was reported by S Dai et al.[20] In addition to the analytical applications of pyrohydrolysis for the soil and geological samples as mentioned above, there are many such studies dealing with the determination of halogens in soil samples, rock, sediment, cement samples etc. where pyrohydrolysis separation was exploited.[21–23] Analysis of halides in magmatic apatites, geochemical reference materials and clay samples were also reported with pyrohydrolysis separation.[24–28] Quantitative separation of halides from soil and rock samples by pyrohydrolysis is difficult and the same was shown by comparing with neutron activation analysis.[23]

Analysis of coal

Pyrohydrolysis has been proved to be an effective and reliable method for the separation of iodine from coal and other geological materials as it provides the sample free from matrix as well as from the excess regents added. Since coal is a combustible organic medium with significant sulphur content, it requires controlled combustion with appropriate oxygen flux to avoid deflagration as well as the formation of sulphorus acid. Daishe Wu et al. extensively studied the pyrohydrolytic decomposition of coal for separating iodine. They also studied the variables that can affect the separation and their optimum conditions were identified.[29] B. Peng and et al., determined F, Cl, Br, and I in coal samples by pyrohydrolysis-IC, where pyrohydrolysis conditions were optimised with a view to obtain better limit of detections (LODs) for F, Cl, Br and I.[30] Sredovi`ca et al. determined fluorine in lignite coal in order to understand the corrosion effects of F in thermal power plants and its environmental impact. They evaluated the pyrohydrolysis parameters and optimised by using two statistical approaches. further quantification of fluoride in the pyrohydrolytic distillate was carried out FISE method.[31] Pyrohydrolysis separation of fluorine in super-high organic sulphur coals was also reported.[32] The Br and I in raw coal, bottom ash (BA) and fly ash (FA) from seven thermal power plants (TPP) were determined using pyrohydrolysis separation followed by ICP-MS analysis.[28] Pyrohydrolysis is extensively used in certifying the newly developed reference materials[33] and also in the determination of halogens in fossil fuels[34] and petroleum samples such as crude oil.[35]

Isotopic composition of halides

Interesting work on the determination of isotopic compositions of halogens (I and Cl) were reported where pyrohydrolysis separation played an important role in obtaining a clean sample suitable for the mass spectrometric analyses. Determination of $^{129}I/^{127}I$ in fish samples has been reported and the method had an advantage of very low background.[36] M. N. Herold et al., used pyrohydrolysis for a similar separation of ^{129}I and ^{127}I from organic rich soil matrix.[37] ^{129}I was determined in Fukushima and Chernobyl soil samples by following pyrohydrolysis-ICPMS method.[38–40] Pyrohydrolysis was also applied for the determination of Cl isotopes, as Cl isotopes are considered as tracers for geochemical processes.[41]

Environmental and biological samples

Applications of pyrohydrolysis were extended to the analysis of biological and environmental samples. Pyrohydrolysis separation of Br and I in airborne particulate matters collected on a glass filter was reported.[42] Another work deals with the separation of Br, F and I in medicines and in some mineral supplements.[43] In both the cases quantification was achieved with ICP-MS. Determination of iodine was carried out in food materials, where the separation of iodine was investigated with a stepwise temperature conditions.[44] The research articles on the pyrohydrolysis of nano particles were also reported.[45–47]

Pyrohydrolysis in nuclear industry

The nuclear materials like, nuclear fuels, cladding materials, neutron poisons, reflectors, control rod materials (both finished products and starting raw materials) etc. has stringent specification limits for F, Cl and B. For instance the maximum permissible limit of Cl and F in oxide and carbide fuels are 15 and 25 µg/g respectively. This is because fluorine and chlorine are corrosive elements and their presence in the above materials would initiate corrosion of both structural and fuel elements. Boron on the other hand is a neutron poison as it has high neutron cross section. Like halogens boron is also amenable to pyrohydrolysis separation.[9] Pyrohydrolysis is being used on routine basis to separate halogens and boron simultaneously from nuclear materials.[48] Since pyrohydrolysis has the advantage to handle the radioactive materials safely and it provides a sample solution free from radioactive matrix elements like Pu etc., it is widely employed for separating halogens and boron in nuclear fuels and associated materials. For example, separation of chlorine and fluorine from Pu-alloys and (U, Pu) C samples are achieved only by pyrohydrolysis. Determination of fluoride and chloride in radioactive liquid wastes was also reported wherein the separation was carried out by pyrohydrolysis by mixing the liquid sample with a pre-analysed holding material (U_3O_8 powder).[49] Thorium oxide, an important nuclear material, is a refractory material and difficult to pyrohydrolyse. A pandey et al.[50] had studied the pyrohydrolytic behaviour of thoria using different accelerators (V_2O_5, WO_3 and MoO_3). An application of x-ray fluorescence method for determining chlorine in pyrohydrolytic distillate of (U, Pu) C has been reported.[51]

Metallic fuels such as U-Zr and U-Pu-Zr alloys are the proposed fuels for the fast breeder reactors and determination of halogens in these fuels also carried out by pyrohydrolytic separation. The study also showed in addition to the pyrohydrolisability, the matrix opening is also a crucial factor for achieving the complete recovery of halogens.[52] An ion chromatographic study deals with the separation and identification of pyrohydrolysis products of (U, Pu) C has been reported[53] and the study further reported that the pyrohydrolytic conditions are responsible for the formation of organic acids during the pyrohydrolysis of metal carbides. Another study reports about the pyrohydrolytic separation of boron in U_3Si_2 required for the determination of isotopic composition of boron by ICP-MS.[54] Pyrohydrolysis was used for generation of zirconia from ZrF_4.[55] Jia Peng et al., studied the pyrohydrolysis behaviour of SmF_3 with a view to address the issues related to thorium based molten salt reactor fuels.[56] Recently feasibility on the pyrohydrolytic separation of molybdenum as its volatile oxide has been explored for the first time. Mo present in a matrix can be oxidised to its oxide MoO_3 (with high vapour pressure), further the vapour pressure of the oxide increases drastically in presence of moist environment. Based on these observations, a novel method of pyrohydrolysis for separating Mo from uranium matrix was established.[57] The study describes about the necessary conditions for pyrohydrolysis and the modifications incorporated in the pyrohydrolysis apparatus for achieving complete recovery of Mo.

Miscellaneous applications

Apart from above applications, pyrohydrolysis has been used to separate halogens from cardboard[58] and iron ore.[59] It was also used for regeneration of spent pickling solution.[60] During steel production HCl is used to remove the oxide layer on the surface and this pickling solution after use was regenerated using pyrohydrolysis. S Zhou et al. have shown the use of pyrohydrolysis to generate HCl from NaCl for chlorination of nickel and iron oxides.[61] Pyrohydrolysis was applied in the determination of halogens in glass reference materials (BHVO-2G, BIR-1G, BCR-2G, GSD-1G, GSE-1G, NIST SRM 610 and NIST SRM 612).[62] In the determination of halides in glass standards the pyrohydrolysis distilates were analysed by Ion Chromatography and X-ray fluoresence techniques.

Conclusion

Pyrohydrolysis is widely used for the separation of halogens, sulphur and boron directly from different types of samples. It provides a sample solution free from matrix and therefore, considered to be a clean separation method. Although it is known as an old methodology, its scope gets expanded every year due to its applications in diverse fields.

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Conflict of interest

The author declares there is no conflict of interest.

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