Study of the Possibility of Rhenium Extraction and Preconcentration from Plants

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Abstract: - Investigation was carried out on leaves of green geranium (*Pelargonium)* grown on soil spiked with perrhenate and containing a known amount of bioaccumulated rhenium. Two ways of rhenium extraction and preconcentration from green leaves of geranium were studied: i) direct incineration of the raw leaves and alkaline leaching of rhenium from the ash; ii) ethanol extraction of rhenium from raw leaves followed by evaporation of ethanol, ashing of dry residue and alkaline extraction of rhenium from the ash. It was found possible to concentrate rhenium 24 444 times (as compared to its initial concentration in soils) using ethanol extraction from green plant mass in the remaining ash. A better (in comparison with the case of direct incineration of raw leaves) preliminarily purification of the leaching alkaline solutions from major ash cations (K, Ca, and Mg) was achieved by ethanol extraction of rhenium. The investigation revealed that it was possible to develop a cheap and environmentally friendly biotechnology for rhenium recovery from soils and waters using plants.

Key-Words: - Rhenium, Plants, Green geranium, Extraction, Preconcentration, Purification

1 Introduction

It is known that rhenium is accumulated in a natural way in plants growing in ore dressing and metallurgical processing regions in concentrations many times exceeding its natural or background occurrence (1). Our previous studies have shown that the plant biosphere from these regions is a natural biocollector and concentrator of dispersed rhenium [2, 3, and 4]. The basic advantage of Re is that this metal is preferably accumulated (more than 98%) in green over ground parts of all kinds of plants. It is very easy to harvest the green plant mass containing rhenium and reduce it to ash by incineration. The aim of the present study is to develop a procedure for effective extraction and preconcentration of rhenium from plants.

2 Main problems of rhenium extraction from plants

In our previous study we developed three procedures for extraction of rhenium from plant material with a view to its subsequent quantitative determination according to a catalytic N, N-Dimethyldithiooxamide (DMDTO) spectrophotometric method [5]. They include: i) a laboratory variant based on incineration of plant material in the temperature range 420-490^{o}C and extraction of rhenium from the ash with hot and cold 6.5 % NH_4OH or 1 mol l^{-1} NaOH solutions; ii) extraction of Re together with chlorophyll and other dyes from the green plant by hot ethanol, evaporation of ethanol, destruction of the organic dyes either thermally or with HCl, and extraction of Re with NaOH or NH_4OH solutions; iii) direct extraction of rhenium from the green leaves by HCl, alkalization of the acid extract, destruction of the organic matter with H_2O_2 under heating. We chose the first two procedures because the third one includes many operations, which complicates the rhenium extraction and is not suitable to be applied as technological procedure.

Incineration of plants is the usual manner for preconcentration of metals in ash. The resulting ash contains rhenium, main ash mineral elements and a small quantity of not completely oxidized carbon. It is known that perrhenate is quantitatively retained on active carbon and can be further eluted with hot or cold alkalis [6]. Using the alkaline solutions we extract quantitatively rhenium from the ash, but the leaching alkaline solution also contains some quantity of ions of basic ash elements such as Ca, K,

Mg, Na, Si and Fe. It is very important to determine the content of these elements in the leaching alkaline solution and to find a suitable and simple procedure for reduction of the impurities. The present study is also aimed at retracing the degree of rhenium concentration in ash obtained by different methods.

3 Study of the possibility of rhenium preconcentration and extraction from leaves of green geranium

Experiments were carried out with a plant sample (leaves of green geranium) with known Re content prepared as follows [2]:

1 kg dry soil (in a pot) with planted green geranium was spiked with 1000 μg Re as $KReO_4$ solution. The plant was regularly watered. Leaves were analyzed for Re content according to a highly sensitive and selective catalytic method for rhenium determination with N, N-Dimethyldithiooxamide [7]. The results showed that bioaccumulated Re was distributed uniformly in all leaves. In one week the Re content appeared to be 20 μg Re per g raw leaves while in three weeks the content of metal increased to 110 μg Re per g raw leaves and did not increase any more with time. The Re concentration in the leaves of green geranium remained constant during six months. All further experiments were carried out with these leaves.

3.1 Extraction of rhenium from the green mass by incineration.

The ashing of samples was carried out as follows: 1 g of raw green leaves of geranium was incinerated at a temperature of 480°C. The weight of the resulting ash was 0.012 g. It contained rhenium and the main ash elements (such as Ca, Mg, K and others) as well as some particles of carbon resulting from incomplete oxidation of the organic matter. To extract the rhenium the ash was treated with 5 portions of 2 ml 6.5 % NH_4OH each. The resulting alkaline solution was turbid because of the formation of insoluble hydroxides and carbonates of some of the ash elements. By filtration of the turbid solution through a filter paper (medium pore size), we reduced the concentration of the ash elements in the leaching solution (insoluble hydroxides, carbonates and carbon particles which were retained on the filter paper). The clear filtrate was analyzed for rhenium content by a catalytic method [7], and for concentrations of Ca, K and Mg, by FAAS. The results of the analyses are shown in Table1.

3.2 Extraction of rhenium from green leaves by hot ethanol

Rhenium was extracted from green geranium leaves by hot ethanol using the following procedure: 1 g raw finely cut green leaves of geranium were placed in a quartz beaker and a 10 ml portion of ethanol was added. The mixture was heated with an IR lamp to boiling. The green extract containing chlorophyll and other leaf dyes was decanted and a fresh 10 ml portion of ethanol was added. The mixture was again heated with an IR lamp until boiling. The second extract was added to the first one. The procedure was repeated until the leaves became colorless. The combined ethanol extracts were evaporated to dryness (IR lamp). The resulting brown dry residue was ignited in a furnace at 480°C. The ash weight was 0.0045 g. Rhenium was extracted from the ash with 5 portions of 6.5 % NH_4OH 2 ml each one as described above. The resulting solution was analyzed for rhenium content by a catalytic method [7] and for Ca, K and Mg content, by FAAS. The results of the analyses are shown in Table 1.

4 Results and discussion

Table 1 Concentrations of Re, Ca, Mg and K in ash obtained by different procedures

Elements	$C_{element}$ in μg/g ash	
	Manner of sample treatment	
	Incineration of raw leaves	Extraction of Re by hot EtOH, evaporation of EtOH, incineration of dry residue
Re	9 167	24 444
Ca	13 052	8 626
Mg	457	287
K	184 200	51 758

4.1. Degree of rhenium preconcentration in ash

The results in Table 1 show that on incineration of 1 g raw leaves of green geranium, the concentration of rhenium has increased from 110 μg/g raw leaves up

to 9 167 μg Re/g ash i.e.83 times. When rhenium is extracted by hot ethanol, its concentration increases from 110 μg/g in the raw leaves up to 24 444 μg/g ash, i. e. 222 times. This dependence is in accordance with the reduction of the ash weight against the plant mass. If we retrace the increase of rhenium concentration from soil to raw leaves and from raw leaves to ash it is seen that initially rhenium is concentrated in plants in a natural way more than 100 times. Incineration of raw leaves results in an about 9167 fold concentration rise, while with ethanol extraction an approximately 24444 fold increase is achieved as compared to the initial Re concentration in soil (1μg Re/g soil). It could be resumed that the results of our study illustrate the efficiency of the simple and environmentally friendly procedure for rhenium extraction from green plants by hot ethanol developed by us. By our procedure we achieve a more than 8 fold Re preconcentration, which is more than the rhenium content in the richest molybdenum concentrates (Stavanger Norway 3100 g Re/ t) [8].

4.2. Degree of purification from ash elements

The results in Table1 also show that the Ca and Mg concentrations in the leaching solution after ethanol extraction of rhenium are approximately 1.5 times lower than those in the leaching solution from direct incineration of raw leaves. For K this reduction is 3.5 times. These results could be explained by the following mechanism of rhenium extraction from fresh leaves with hot ethanol [1]. When the leaves are in contact with ethanol, the lysis takes place in the cell, because of its being introduced to a more concentrated medium than that in the cell sap. The resulting reaction of the cell is its shrinking because of the diffusion of water containing the dissolved mineral substances (including perrhenate ions) to the environment. The turgor pressure in the cell is reduced to zero and the cell is destroyed. After the evaporation of ethanol, the remaining dry residue contains only soluble mineral substances and polar organic matter from the cell sap. During the incineration of dry residue the organic matter is oxidized and the ash contains only mineral elements from the cell sap. By this pretreatment we reduce the content of ash elements in the leaching solution. On the contrary, with direct incineration of raw leaves the ash contains the total concentration of mineral elements from the leave mass.

5 Conclusion

We investigated two possibilities for extraction and concentration of rhenium from green plants. We have found that:

- with direct incineration of raw leaves rhenium is preconcentrated 83 times in the ash;
- by ethanol extraction of rhenium from raw leaves followed by its evaporation (distillation) and incineration of the dry residue, rhenium is preconcentrated 222 times in the ash because of the reduction of the ash mass;
- use of alkaline solution for rhenium extraction from ash leads to partial purification of the leaching solution from some ash elements (formation of insoluble hydroxides and carbonates);
- by ethanol extraction of rhenium from raw leaves additionally purification of the leaching solution from impurities is achieved

Based on the results, it may be concluded that extraction of rhenium from raw leaves by hot ethanol is better for its recovery than is direct incineration of plant mass.

The above approaches could be used for developing a simple and environmentally friendly technology for rhenium recovery from plants.

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