

Recovery of molybdenum, phosphorus and arsenic from leaching solution of molybdenum residues by solvent extraction with primary amine and tributylphosphate

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Abstract— Effective extraction and separation of molybdenum, phosphorus and arsenic from aqueous and leaching solutions of molybdenum residues was studied using low concentration of primary amine and tributylphosphate as solvents at the optimum acidity of pH 6–7. The loaded organic phase was stripped with NaOH solution with high O/A phase ratios, and the resultant aqueous solution containing high content of molybdenum, phosphorus and arsenic was acidified and sodium salts of 12 - molybdophosphate or 12 - molybdoarsenate can be obtained. The extraction mechanism was investigated using chemical analysis, UV and IR spectra as well as molar conductance determination. It was found that molybdenum, phosphorus and arsenic was extracted into organic phase as 5 - molybdodiphosphoric acid and 6 - molybdodiarsenic acid by solvation mechanism with the formation of hydrogen bond between heteropolyacids, primary amine and tributylphosphate. However, the extracted species exist in organic phase as ion - associated species. It was proposed that the transfer of proton from heteropolyacids to primary amine in extracted species occurs intramolecularly resulting to the formation of ion - associated species because primary amine is a weak base and heteropolyacids are strong acids.

Keywords: molybdenum; arsenic; phosphorus; solvent extraction; molybdenum residues.

1 Introduction

The removal of phosphorus, arsenic and silica as impurities from alkaline leaching solutions is an important step in hydrometallurgy of tungsten and molybdenum. The traditional and effective method used in industry is by precipitation with the addition of magnesium salt to the leaching solution. However, this process has many problems such as low recovery of metals, complex

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impurities separation flow sheet, especially difficulty to dispose of large amount of the precipitate generated and pollution arising from the storage of it (Zhao, 1993).

So far, there are no effective and economic approach developed to treat and detoxify these residues which contain toxic substances of arsenic and phosphorus as well as valuable metal of molybdenum. At present, nearly all the residues are simply stored as common solid waste and put on the ground. The leaching solution of residues generated by rainwater or surface water usually contaminate the underground water. It is obvious that the treatment and detoxification of molybdenum residues is urgent in both aspects of pollution control and resources reclamation of molybdenum.

In our preliminary work, the residues was leached with mineral acids and satisfactory results were obtained. Phosphorus, arsenic and molybdenum in the residues can nearly be leached quantitatively and the resultant slags can be considered to be nontoxic and nonharmful to the environment. In this paper, only the separation and recovery of phosphorus, arsenic and molybdenum from the leaching solutions were reported.

Few reports on the extraction of phosphorus and arsenic from aqueous solutions can be found in literature. However, the extraction and separation of heteropolyacids of phosphorus and arsenic has been studied extensively in analytical chemistry with various extractants such as Alamine 336, MIBK, D₂EHPA and TBP. Nearly all the solvent extraction processes developed for the separation of heteropolyacids of phosphorus and arsenic were carried out in strong acidic medium with high cost and low extraction efficiency.

In our other reports, it has been found that primary amine and tributylphosphate can be used for the effective extraction and separation of heteropolyacids of phosphorus, arsenic and tungsten (Zhao, 1991; 1992; 1993). Further experiment found that molybdoheteropolyacids of phosphorus and arsenic can also be extracted effectively by this solvent system, and was developed for the separation and recovery of phosphorus, arsenic and molybdenum from aqueous or leaching solution of molybdenum residues in this work.

2 Experimental

A mechanical shaker with about 60 oscillations per minute was used to mix aqueous and organic solutions at room temperature. In order to observe the extractability of phosphorus, arsenic and molybdenum from leaching solutions of molybdenum residues, the aqueous phase used in the experiments was prepared by sodium salts of arsenic, phosphorus and molybdenum. The results were justified with leaching solution of molybdenum residues. A volume of 10 ml or both aqueous and organic solution was used in the experiments unless it was indicated in the text. The initial pH value of aqueous phase was adjusted by sulfuric acid solution and the equilibrium pH value was determined after the extraction operation was completed. The difference between initial and equilibrium pH value was found to be about 0.7 when 1% primary amine in organic phase was used as extractants. The concentrations of primary amine and tributylphosphate (TBP) in organic phase were expressed as volume percent. 1% primary amine is equal to 30.43 mmol/dm³. Primary amine with a total carbon number of about 19–21 (R₁R₂CHNH₂ or simplified as RNH₂ for

brevity in the following expressions) was supplied by Institute of Organic Chemistry, Chinese of Academy of Sciences, Shanghai, and was purified by distillation. Commercial kerosene was used as diluent. The other chemicals are of analytical grade purity. The colorimetric determination of phosphorus, arsenic and molybdenum and UV spectra of loaded organic phase were carried out in 1 cm cells with HP - 8541A spectrophotometer made by Hewlett - Parkard Company (USA).

The experimental results showed that two or three minutes of shaking were enough to approach the extraction equilibrium of all experiments involved while less than one minute for the stripping of loaded organic phase.

Phosphorus and arsenic were analyzed colorimetrically with molybdenum blue solution and molybdenum with NH_4SCN methods.

3 Results and discussion

3.1 Effect of acidity of aqueous solution

The extraction of phosphorus and arsenic is strongly dependent on the acidity of aqueous phase as shown in Fig. 1. The optimum pH value was determined to be about 6.5. However, in the following experiments, the extraction acidity was chosen at the range of equilibrium pH 6—7 because it is difficult to keep the equilibrium pH value at 6.5 for all the extraction operations.

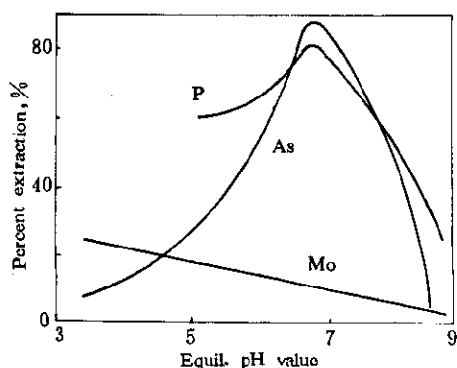


Fig. 1 Dependency of extraction and separation of P, As and Mo from aqueous solutions on equilibrium pH value Mo 40 g/dm³; P 262 mg/dm³; As 242 mg/dm³; 18°C; 1% RNH₂ + 10% TBP in kerosene-solution

3.2 Effect of molybdenum concentration

The concentration of molybdenum in leaching solution of molybdenum residues is usually low, ranged from 1 to 10 g/dm³. The experimental results showed that phosphorus and arsenic can not be extracted and separated from aqueous solution without the presence of molybdenum in aqueous phase. This is one of reason to propose that phosphorus and arsenic was extracted into organic phase as heteropolyacids. Fig. 2 gives the relationship between the extraction and initial concentration of molybdenum in aqueous solution. It can be seen that extraction of phosphorus and arsenic increases remarkably as the increase of molybdenum content in aqueous phase, and the extraction reaches the maxi-

imum value when the molybdenum concentration is higher than 5 g/dm³ under the conditions of Fig. 2. In general, the initial molybdenum content in aqueous solution should be high enough to make $\text{Mo/P} > 2.5$ and $\text{M/As} > 3$ simultaneously in order to obtain the optimum extraction of phosphorus and arsenic. In the following experiments, a molybdenum content of 40 g/dm³ in aqueous phase was used.

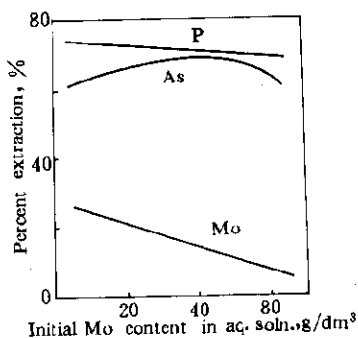


Fig. 2 Effect of Mo concentration in aqueous phase on the extraction of P and As with 1% RNH_2 + 10% TBP in kerosene solution

P 263 mg/dm^3 ; As 242 mg/dm^3 ; 17°C; pH 6.5

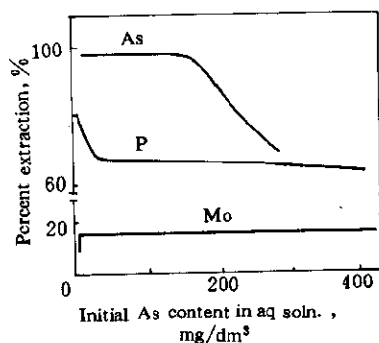


Fig. 3 Effect of As concentration in aqueous phase on the extraction of P and As with 1% RNH_2 + 10% TBP in kerosene solution

P 263 mg/dm^3 ; Mo 40 g/dm^3 ; pH 6.4; 17°C

3.3 Effect of phosphorus and arsenic content

The extraction of phosphorus and arsenic is competitive. It is a function of phosphorus and arsenic concentration in aqueous phase, pH value and content of primary amine in organic phase. When the content of arsenic in aqueous phase is lower than 150 mg/dm^3 , the arsenic can be extracted quantitatively while the extraction of phosphorus decrease and that of molybdenum increases slightly as the increase of arsenic content in aqueous solution as shown in Fig. 3. If the concentration of arsenic keeps unchanged while the phosphorus content in aqueous solution increases, the percent extraction of both phosphorus and arsenic decreases as given in Fig. 4.

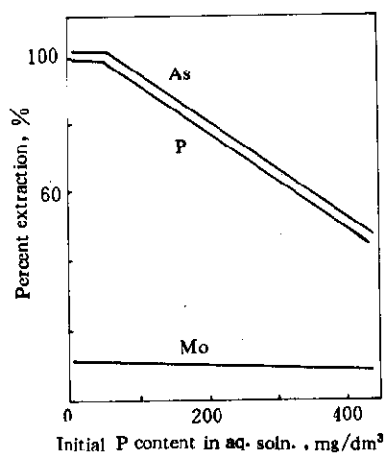


Fig. 4 Effect of P content in aqueous solution on the extraction of P and As with 1% RNH_2 + 10% TBP in kerosene solution

As 242 mg/dm^3 ; Mo 40 g/dm^3 ; pH 6.3; 16°C

3.4 Effect of primary amine and tributylphosphate (TBP) concentration and phase ratios (O/A)

From the experimental results mentioned above, it can be seen that when phosphorus and arsenic content in aqueous phase increases to some extent, the phosphorus and arsenic can not be extracted quantitatively. However, if the content of primary amine and TBP in organic phase in-

creases, the extraction of phosphorus and arsenic as well as molybdenum will increase considerably as shown in Fig. 5. For example, when the concentration of primary amine in organic phase increases from 0.2% to 5%, the extraction of phosphorus and arsenic increases from 58 to about

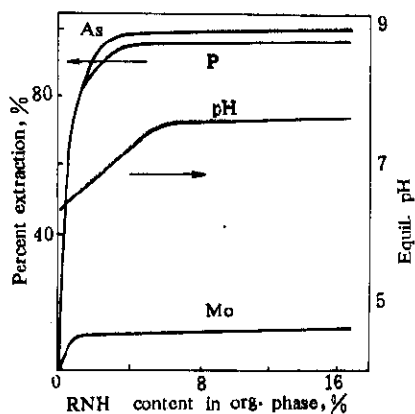


Fig. 5 Relationship between the content of RNH_2 in organic phase and the extraction of P and As with 10% TBP in kerosene solution
P 262 mg/dm^3 ; As 242 mg/dm^3 ; Mo 40 g/dm^3 ,
12°C

was less than 10%. Moreover, the loaded organic phase may appear the precipitate without the presence of TBP (Table 1). The optimum TBP concentration in organic phase was determined to be about 10%.

100% respectively under the condition of Fig. 5. In addition, it can be seen that the equilibrium pH increases as the increase of content of primary amine in organic phase because the extraction is carried out at the same initial pH value of 6.0. The content of primary amine in organic phase should be chosen according to the concentration of phosphorus and arsenic as well as molybdenum in aqueous solutions. If the content of primary amine in organic phase is higher than 20%, the extraction power will decrease because of the formation of hydrogen bonding between primary amine molecules.

The addition of TBP to the organic phase can increase the extraction of phosphorus, arsenic and molybdenum if the content of TBP

Table 1 The relationship between the extraction of phosphorus, arsenic and molybdenum and the content of TBP in organic phase

Content of TBP, %	Extn. of P, %	Extn. of As, %	Extn. of Mo, %
0.0	70.2	58.9	9.8
5.0	81.6	90.1	9.7
10.0	82.1	91.2	9.8
15.0	75.5	80.3	9.9
20.0	72.8	78.9	9.7
40.0	70.0	75.1	9.5

Note, P 262 mg/dm^3 ; As 242 mg/dm^3 ; Mo 40 g/dm^3 ; RNH_2 1%; 12°C,

When the content of TBP is from 0.0 to 4%, the precipitation occurs in organic phase during the extraction operations

The extraction and separation of phosphorus, arsenic and molybdenum increase as the increase of phase ratios (O/A) as shown in Fig. 6. The experimental results indicated that the third phase may appear if the phase ratio is higher than 4. In the practical application, the effective extraction may be obtained by increasing either phase ratio or concentration of primary amine. A phase ratio of less than 4 and concentration of primary amine less than 20% was recommended.

3.5 The extraction of molybdenum

The extraction of molybdenum increases as the decrease of pH value and the optimum extraction may be obtained at acidic medium (Zhao, 1992). If the content of molybdenum in aqueous phase is high and can not be extracted completely with phosphorus and arsenic, the remained molybdenum in aqueous phase should be extracted again with primary amine and TBP if necessary.

3.6 The stripping of loaded organic phase

The loaded organic phase can be stripped with NaOH solution and the quantitative stripping can be obtained if the pH value in aqueous stripping solution is higher than 8.5 as shown in Fig. 7. The loaded organic phase can be stripped with high phase ratio (O/A) to increase the content of phosphorus, arsenic and molybdenum in aqueous solution. For example, the content of phosphorus, arsenic and molybdenum in leaching solution is 120 mg P/dm³, 150 mg As/dm³ and 5g Mo/dm³ respectively, which is extracted with a phase ratio of 4 and then stripped with a phase ratio of 10, the resultant aqueous stripping contains 4800 mg P/dm³, 6000 mg As/dm³ and 200g Mo/dm³ respectively. The solution can be acidified and extracted with ether, 12 - molybdophosphoric acid and 12 - molybdoarsenic acid will be obtained readily.

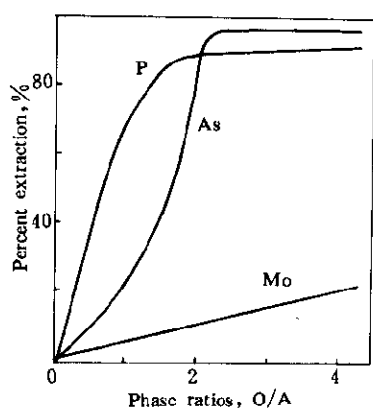


Fig. 6 Effect of phase ratio (O/A) on the extraction of P, As and Mo from aqueous solution with 1% RNH₂ + 10% TBP in kerosene solution
Mo 40 g/dm³; As 243 mg/dm³; P 262 mg/dm³;
pH 6.5; 12°C

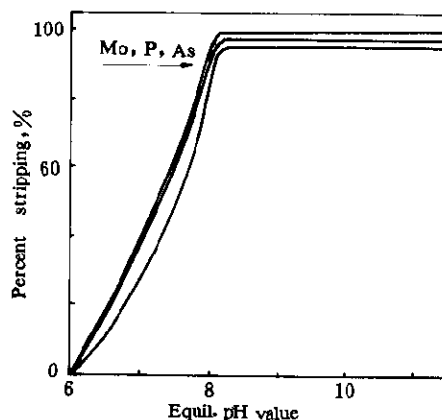


Fig. 7 Stripping of loaded organic phase with 0.1 mol/dm³ NaOH solution
Phase ratio (O/A) = 1:1; Composition of loaded organic phase; P 163 mg/dm³; As 279 mg/dm³;
Mo 3.8 g/dm³; 15°C

3.7 The extraction and separation of phosphorus, arsenic and molybdenum from crude leaching solution

The composition of molybdenum residues and their leaching solutions are varied. The typical leaching solution and its extraction results with primary amine and TBP are shown in Table 2. It can be seen that the phosphorus, arsenic and molybdenum in the leaching solution can be also ex-

tracted and separated very effectively. The results are in well agreement with that from the solutions prepared by sodium salts of phosphorus, arsenic and molybdenum.

The composition of crude leaching solution is very complex. However, only the harmful elements such as phosphorus, arsenic as well as molybdenum can be extracted. The other substances such as Ca, Cu, Fe, Al, Mn, can not be extracted. The extraction of Si (as molybdosilicic acid) is negligible in comparison with that of phosphorus and arsenic.

Table 2 The typical composition of crude leaching solution of molybdenum residues and its extraction and separation of phosphorus, arsenic and molybdenum with primary amine and TBP as solvents

1 Effect of equilibrium pH value

Equil. pH	Mo extn. , %	P extn. , %	As extn. , %	Si extn. , %
7.38	30	90	88	20
6.90	40	95	90	30
5.87	50	99	98	35

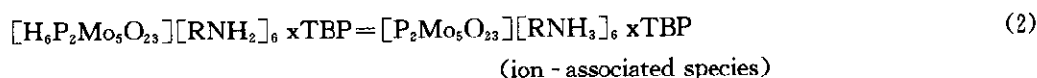
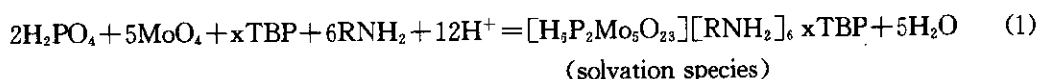
2 Effect of P, As and Si added to the aqueous phase

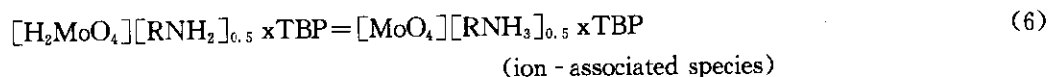
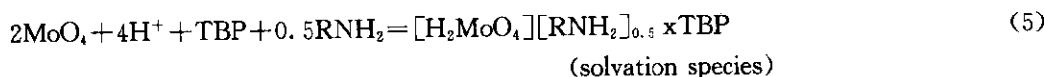
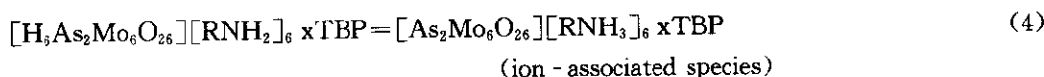
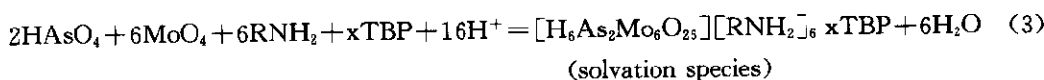
Equil. pH	7.02	5.96	6.93	6.86	7.04	6.94
P added, mg/dm ³	99	208	208	208	0	0
Total P in aq. soln. , mg/dm ³	219	328	328	328	120	120
As added, mg/dm ³	0	0	206	208	0	0
Total As in aq. soln. , mg/dm ³	150	150	356	356	150	150
Si added, mg/dm ³	0	0	0	84	60	133
Total Si in aq. soln. , mg/dm ³	80	80	80	164	140	213
P extn. , %	64	44	28	24	92	92
As extn. , %	87	73	31	32	90	90
Si extn. , %	13	18	13	14	23	14
Mo extn. , %	40	35	40	45	35	44

Composition of crude leaching solution (mg/dm³): P 120; As 150; Mo 10000; Si 80; Cu 100; Fe 1000; Ca 2000; W 100; Zn 50; pH>12; Organic phase: 1% RNH₂+ 10% TBP; 20°C

3.8 Extraction mechanism

The extracted species and extraction mechanism had been studied in detail (Zhao, 1991; 1992; 1993) and were summarized as follows. It was found that phosphorus, arsenic and molybdenum was extracted into organic phase as follows (pH 6–7):





Because the loaded organic phase may contain the extracted species of phosphorus, arsenic and molybdenum simultaneously, the extracted species were determined from two - component systems such as Mo - P, Mo - As, or pure molybdate solutions. The molar ratios in the extracted species were obtained based on the Mo/P, RNH₂/P, Mo/As and RNH₂/As in the loaded organic phase as shown in Table 3 and Table 4. The heteropolyacids or anions showed above have been studied in detail. These acids or anions are found to be stable in pH 5—7 (Pope, 1983) and their corresponding chemical formula are used in (1) — (5). It was proposed that the loaded organic phase was saturated and all the primary amine was combined to form extracted species when the molar ratios of Mo/P, RNH₂/P, Mo/As and RNH₂/As keep unchanged.

Table 3 The Mo/As and RNH₂/As molar ratios in loaded organic phase with 1% RNH₂ + 10% TBP in n - heptane solution at pH 6.5

No.	1	2	3	4	5
As concn. , g/dm ³	1.12	2.24	3.36	5.50	6.60
Mo/As in org. phase	5.2	3.3	3.0	3.0	3.0
RNH ₂ /As in org. phase	4.2	3.7	3.0	3.0	3.0

Mo 40 g/dm³

Table 4 The Mo/P and RNH₂/P molar ratios in loaded organic phase with 1% RNH₂ + 10% TBP in n - heptane solution at pH 6.5

No.	1	2	3	4	5
P concn. , g/dm ³	3.7	4.2	5.0	6.0	6.9
Mo/P in org. phase	2.58	2.66	2.51	2.38	2.67 (Av. = 2.56)
RNH ₂ /P in org. phase	3.1	2.9	3.0	3.2	3.0

The UV and IR spectra of saturated loaded organic phase is shown in Table 5. It was found that the primary amine in organic phase exists as ion species of [RNH₃]⁺. The IR absorbtion of P=O in TBP was much stronger in the extracted species than that in free TBP molecules, but no shift can be found. The maximum absorbtion of Mo - extracted species in UV spectra was found to be 245 nm which disappeared in the saturated loaded organic phase of phosphorus or arsenic extracted species. It can be proposed that in saturated organic phase, no extracted species of Mo exists and the composition of extracted species of phosphorus and arsenic can be proposed to be just the same as shown in (1) — (4).

Table 5 IR and UV spectra of loaded organic phase

	Systems	Frequencies or wavelength	Assignment
IR	1% $\text{RNH}_2 + 10\%$ TBP	3150 cm^{-1} , w	RNH_2 , N-H
	in n-heptane	1240 cm^{-1} , m	TBP, P=0
	Loaded org. phase	3000 cm^{-1} , m	RNH_2 , N-H
	Mo/P=2.5 or Mo/As=3	1240 cm^{-1} , s	TBP, P=0
UV	1% $\text{RNH}_2 + 10\%$ TBP	230 nm, s	
	in n-heptane soln.	270 nm, m	
	Loaded org. phase	310 nm, s	
	of only Mo	245 nm, m	Absorption of Mo extd. species
	Loaded org. phase	310 nm, s	No absorption
	Mo/P=2.5 or Mo/As=3		at 245 nm

The electric conductance of loaded organic phase in n-heptane solution was determined and the results are shown in Fig. 8. It can be found that the dissociation of extracted species in organic solutions occurs. The molar conductance increases as the increase of concentration of extracted species. The experimental results showed that the dissociation in organic phase increases considerably if the polarity of solvent increases (for example, the n-heptane in organic solution

was removed and TBP was used as diluent for extracted species). It is obvious that the extracted species inorganic solvents is dissociated weakly, which is in agreement with the results of IR spectra.

By considering the generally accepted concept that primary amine exists as neutral molecules at pH 6–7 (Zhao, 1993), it can be proposed reasonably that phosphorus, arsenic and molybdenum are extracted into organic phase by solvation mechanism with the formation of hydrogen bonding between primary

amine, TBP and heteropolyacids. Because the acids are strong acids, and primary amine is a weak base, the transfer of proton from the acids to primary amine occurs intramolecularly to form ion-associated species.

4 Conclusion

Phosphorus, arsenic and molybdenum can be extracted and separated very effectively from

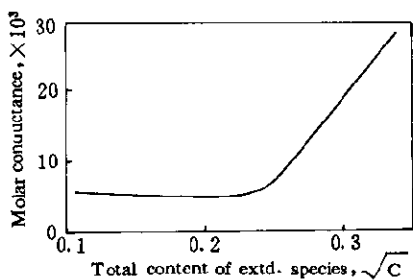


Fig. 8 The relationship between electric conductance and the total concentration of Mo-P and Mo-As extracted species

aqueous and crude leaching solution of molybdenum residues by solvation mechanism with primary amine and TBP as solvents. The composition of extracted species was determined and the loaded organic phase was characterized with IR, UV spectra, electric conductance determination and chemical analysis.

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