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New XRS Procedure

By

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To indicate the efficiency of the heavy dilution procedure those samples were analyzed by XRS using U in the coal ash as standards, therefore, no matrix control. The results follow.

MATRIX	% U TAKEN	% U FOUND	RECOVERY
$NaHCO_3$	0.950	1.94	204%
Fe_2O_3	0.950	0.165	17%
PbO_2	0.950	0.040	4%

We are saying that 0.950% uranium in $NaHCO_3$ looked like 1.94%U, in Fe_2O_3 it looked like 0.165%U, and in PbO_2 it looked like 0.040%. This shows the magnitude of error associated in XRS analyses with nearly maximum matrix effects and no matrix control. A comparison of these data to that of the inert dilution method shows the remarkable matrix control obtained with the dilution method.

Tin analyses by the dilution method was then studied. Standards of tin in widely varying matrixes and at various levels were prepared. The samples were analyzed by the dilution method and by comparing to standards of tin in quartz (no matrix control). The results follow:

MATRIX	% Sn TAKEN	% Sn FOUND	RECOVERY	% Sn COMPARED TO QUARTZ MATRIX STDS
$NaHCO_3$	0.875	0.907	104%	1.35
Fe_2O_3	0.875	0.894	102%	0.28
PbO_2	0.875	0.855	97.8%	0.03
Fe_2O_3	0.875	0.894	102%	----
Fe_2O_3	4.39	4.14	94.4%	----
Fe_2O_3	8.79	8.30	94.5%	----
Fe_2O_3	21.9	20.5	93.5%	----

There seems to be a systematic shift in the recovery from the lightest to the heaviest matrix. However, the degree of control is nothing short of amazing; observe the wild values obtained by comparing only to a quartz matrix where no matrix control is used.

The method is extremely well suited to our application of XRS analysis, i.e., the need for a method that will yield ± 5% accuracy for elements that are difficult to determine by other methods, but which may occur in almost any matrix.

It gives one reason to pause and ask why 50 years of XRS application experience has gone by with the finest physicists and chemists applying their efforts when so simple and direct a solution was present. Needless to say, I intend to pursue this procedure in greater detail and range for its application in our laboratory needs.

NEW   XRS   PROCEDURE

Matrix effects comprise the biggest problem to accurate XRS analyses.
Consequently XRS does best in the rapid analyses of a large number of samples
of small matrix variation. Our use of XRS is the most difficult possible -
any element in any possible matrix and probably only a few samples of a nearly
constant matrix.

In the most recent issue of the journal Analytical Chemistry there appeared
a proposed XRS procedure which is said to essentially eliminate matrix effects
(Rafael Vera Mege, Analytical Chemistry, vol 4, no. 1, p. 42-45). Because
of the attractiveness of Mr. Mege's proposed procedure I set out immediately
to test its application.

The procedure is termed "an inert dilution method." He shows theoretically
that once having determined the absorption effect of a standard diluent for
a given x-ray wavelength then any sample can be analyzed for that element by
dilution with the standard diluent and comparing intensity ratios.

I first examined uranium. Samples were compounded in $NaHCO_3$, Fe_2O_3, and
PbO_2, about the widest conceivable matrix variation, and then determined
the constants and analyzed the samples by his method. The results were in-
conclusive. Acceptable values were obtained in the $NaHCO_3$ and the Fe_2O_3
matrixes but was high in the PbO_2 matrix by a factor of about 2X. Mr. Mege
stated that his method would hold so long as there was "no radical shift of
wavelength distribution" (p. 43). I thought that essentially 100% PbO_2 com-
pared to the lighter matrixes constituted a radical shift in wavelength dis-
tribution. Therefore, a very heavy absorber may be more effective than the
original light (quartz) diluent. Mr. Mege suggests a light absorber.

Uranium in $NaHCO_3$, Fe_2O_3, and PbO_2 was studied using La_2O_3 as a heavy absorber.
The results were extremely favorable as is shown below.

URANIUM WITH La_2O_3 ABSORBER

MATRIX	% U TAKEN	% U FOUND	RECOVERY % FOUND / % TAKEN
$NaHCO_3$	0.950	0.995	104%
Fe_2O_3	0.950	0.998	105%
PbO_2	0.950	0.949	100%