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DETERMINATION OF $^{55}Fe/^{58}Fe$ AND $^{59}Fe/^{58}Fe$ ISOTOPIC RATIOS IN IRRADIATED $Na_2/FeNO/CN/_5/.2H_2O$ BY SSMS*

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A procedure for the measurement of the isotopic composition of Fe in irradiated $Na_2/FeNO/CN/_5/.2H_2O$ samples by SSMS is described. Decomposition with $K_2S_2O_7$, followed by extraction of Fe was necessary to eliminate interferences in the mass spectra. A study of the remaining interferences showed that they were of organic origin from the residual MIBK used for the extraction. The order of magnitude of the $^{55}Fe/^{58}Fe$ and $^{59}Fe/^{58}Fe$ ratios was calculated.

INTRODUCTION

The aim of the present work was the measurement of the isotopic composition of Fe in irradiated $Na_2/FeNO/CN/_5/.2H_2O$ as part of a study on the extension of the /n,γ/ reactions over the natural Fe isotopes present in the compound[1].

*SSMS: spark source mass spectrometry.

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Although SSMS with photographic ion detection is not commonly used for this type of analysis because of its low precision, some attempts were made to perform isotopic abundance ratio determinations without prior sample enrichment on trace impurities[2].

A technique without standard reference materials for the determination of the "new" ^{55}Fe and ^{59}Fe isotopes against the least abundant natural ^{58}Fe, to avoid strong matrix effects that appear working with the other ones, was developed.

EXPERIMENTAL

Equipment

A CEC 21-110-C double focussing mass spectrometer with photographic detection was used. The analysis of the photographic plates was made by the celidometric method described by Desjardins et al.[3].

Procedure

Isobaric interferences on the mass spectra of Fe were expected due to ionized fragments of the original sample, because SSMS is non selective neither in the ionization of the elements nor in the chemical bondings. The first step was the dissolution of the sample in HNO_3 and HCl to obtain a solution of NaCl and $FeCl_3$.

Before the dissolution, a synthetic sample /NaCl:$FeCl_3$ = 1:1/ was prepared followed by deposition of drops of saturated solution of it on the end of gold electrodes shaped as pins and clamped upside down in the electrode holders[4]. To evaporate the water, an IR lamp and air stream were used[5].

The resulting electrodes had a good performance /adherence, ionic yield, etc./ during sparking, but the $/^{23}Na^{35}Cl/$ + ion yield a mass line of the same nominal mass as ^{58}Fe. Thus, different wet oxidative dissolutions of the compound were tried, including the search of a suitable element for the plate calibration by the Churchill two-line method[6]. The obtained mass spectra showed that the digestion was incomplete.

Finally, the calcination and disgregation of the sample with $K_2S_2O_7$ was adopted. The melt was dissolved in HCl acid and the Fe extracted with 4-methyl-2-pentanone /MIBK/ and back-extracted with water. Drops of the aqueous solution were deposited on the mentioned gold electrodes.

14 spectra, each of the irradiated sample and the sample without irradiation were obtained on the same plate. From the observation of this plate it was seen that a doublet appeared at the 55 nominal mass and a weak line at the 59 nominal mass in the irradiated sample and only one line at 55 nominal mass in the nonirradiated sample. By atomic absorption spectroscopy /AAS/ we knew that there were no detectable amounts of Mn or Co in the samples, so we decided to measure with high accuracy the coordinates of these lines on the photoplate, and to calculate the exact masses according to Eq. /1/:

$$Mx = /\sqrt{M}_1 + \frac{d_x - d_1}{d_2 - d_1} M_2 - \sqrt{M}_1//^2 \qquad /1/$$

The obtained values are given in Table 1.

The observed line with mass 55.05 could be an ionized fragment from the residual MIBK: $//CH_3/_2\text{-}CH\text{-}C/^+$.

TABLE 1

Exact mass calculations

Irradiated sample			Non-irradiated sample	
Nom. mass	Distance*	Exact mass	Distance*	Exact mass
54	940.5	53.939	826.5	53.939
55	2742.0	54.94**	-	-
55	2940.5	55.05**	2813.5	55.05**
57	6267.5	56.935	6141.0	56.935
58	8007.5	57.933	7883.0	57.933
59	9748.0	58.94**	-	-

* Distances were measured from an arbitrary origin with a Grant microdensitometer.

** These values were calculated with Eq. /1/. The other are tabulated values, needed in that equation as M_1 and M_2 with their corresponding distances d_1 and d_2.

In order to check this assumption the presence of other possible fragments from the MIBK was investigated. The results of this investigation are summarized in Table 2.

DISCUSSION

From the results, we infer the following:

- The lines corresponding to ^{55}Fe and ^{59}Fe were observed in the irradiated sample. The exact masses of those isotopes are ^{55}Fe = 58.93488, in agreement with the experimental values.
- By AAS we discard the presence of Mn and Co.
- Other lines in the Fe zone were identified as organic fragments from MIBK.

TABLE 2

Possible fragmentation of MIBK

Fragment	Exact mass*	Observation
$//CH_3/_2-CH/^+$	43.06	Present
$//CH_3/_2-CH-CH_2/^+$	57.07	Present, doublet with $^{57}Fe^+$
$//CH_3/_2-CH-C/^+$	56.06	Could not be resolved due to $^{56}Fe^+$
$//CH_3/_2-CH-C/^+$	55.05	Present in the investigated doublet
$/CH_3-CH/^+$	28.03	Present
$/CO/^+$	27.99	Present
$/CH_3-C/^+$	27.02	Present
$/CH_3/^+$	15.02	Present
$/CO-CH_2/^+$	42.01	Present
$/CO-CH_3/^+$	43.02	Present
$/CO-CH/^+$	41.003	Present, doublet with $^{41}K^+$ also present

*The exact masses were calculated from tabulated values[7].

- From the antecedents of the samples it was known that there was ^{55}Mn in the non-irradiated sample but that ^{54}Mn appeared due to the

$$^{54}Fe/n,p/^{54}Mn$$

  reaction and was identified by its characteristic radiation. The formation of ^{55}Mn through the $^{54}Mn/n,\gamma/^{55}Mn$ reaction seems to be unlikely.
- There was ^{54}Mn in the irradiated sample and as we did not see it we can conclude that the extraction with MIBK was largely specific for Fe. All the interferences were from organics.

CONCLUSIONS

Usually, strong systematic deviations occur between isotopic abundance values measured by the SSMS technique. The differences are due to different sources of mass discrimination. So, we can calculate only the order of magnitude of the isotopic ratios.

To perform the calculation, it was first necessary to calibrate the plate with the Churchill two-line method, using the ^{35}Cl and ^{37}Cl lines through all the exposures.

Then, the absorbance values measured for ^{58}Fe, ^{55}Fe, and ^{59}Fe transformed by this curve were plotted in a lg-lg plot as explained by Desjardins et al. The distance between the straight lines obtained for each isotope represents the corresponding isotopic ratio:

$$^{55}Fe/^{58}Fe = 0.09$$
$$^{59}Fe/^{58}Fe = 0.05$$

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