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Impurity Analysis of Domestic $MnSO_4 \cdot H_2O$ Introduced to Manganese Bath Method

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=Abstract=

The manganous sulphate bath method is widely used for measurements of neutron source strength. In this study, the analytical chemistry method based on the argon-supported inductively coupled plasmas emission spectrometry was used for examining the impurity contents of domestic $MnSO_4 \cdot H_2O$, the product of Chemical Industry, to induce $^{55}Mn(n,\gamma)^{56}$ Mn reactions.

From the analytical results, mainly potassium, cobalt, and zinc as well as trace amounts of cadmium, lithium, etc. have turned out to be the relevant impurities absorbing the neutrons, and the fraction of neutrons absorbed by the total impurities was calculated. The value obtained was about 1.37% of the neutrons captured by manganese.

1. INTRODUCTION

The manganous sulphate bath continues to be the preferred method for determining neutron source strength. As illustrated in Fig. 1, in the $MnSO_4$ bath method the induced activity is monitored as a measure of the neutron source strength which means the average neutron emission rate per second from a radioactive neutron source. In order to achieve the highest accuracy with this method, it is necessary to perform a complete quantitative elemental impurity analysis of the manganous sulphate($MnSO_4 \cdot H_2O$).

Impurities which absorb neutrons and produce measurable activity would introduce a time dependent bias to the result which would be very difficult to interpret. The impurities in the $MnSO_4 \cdot H_2O$ are present in quantities proportional to the manganese concentration. Therefore, they contribute a

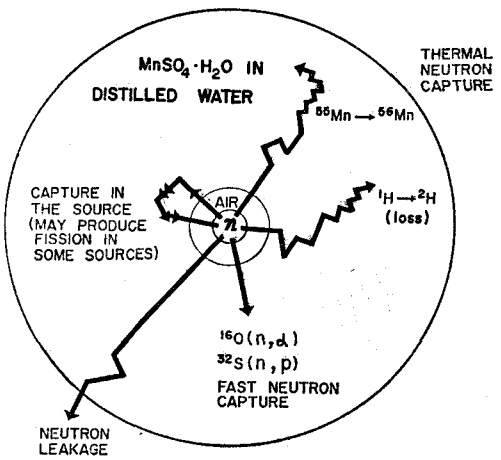

Fig. 1. Schematic diagram of the principle of $MnSO_4$ bath method.

constant fractional error into the N_H/M_{Mn} ratio determination. Any allowance for the impurities in the $MnSO_4$ solution produces higher values for N_H/N_{Mn} ratio and a lower value for the cross section ratio of the hydrogen to the manganese and hence influences comparisons with the published value of σ_H/σ_{Mn}. Allowance for the neutron absorption properties of the impurities affects the whole fitting procedure and produces different values for both the source strength and the cross section ratio.

2. CHANGES TO THE FITTING PROCEDURE

The source strength, Q, of the neutron source is derived from the following well known epuation:

$$Q=\frac{A_S}{\varepsilon.f.(1-L).(1-S).(1-O)} \quad (1)$$

where A_S is the saturation count rate of the ^{56}Mn measured by the bath detector system, ε is the counting efficiency, L is the fractional neutron escape from the boundaries of the bath, S is the fraction of neutrons recaptured by the source and its mounting assembly, O is the fraction of neutrons captured in the (n,α) and (n,p) reactions with oxygen and sulphur, f is the fraction of the remaining neutrons captured by manganese in the absence of impurities and is given by[1]

$$f=\frac{N_{Mn}\sigma_{Mn}(1+G\bar{r}s)_{Mn}}{N_{Mn}[\sigma_{Mn}(1+G\bar{r}s)_{Mn}+\sigma_S+4\sigma_O]+M},$$

$$M=N_H(\sigma_H+0.5\sigma_O) \quad (2)$$

where N_{Mn}, N_H are the concentrations of manganes of manganese and hydrogen nuclei per cubic centimeter in the $MnSO_4$ solution, respective and σ_{Mn}, σ_S, σ_H, σ_O are the thermal neutron capture cross sections of manganese, sulphur, hydrogen, and oxygen. respective The factor $1+G\bar{r}s$ allows for the resonance capture in manganese. In the notation of Westcott et al.[2], S is the parameter representing the resonance activation integral normalized to the thermal neutron capture cross section and $\bar{r}$ is an effective value of the spectral index r averaged over the bath system, G is the resonance self shielding factor for the $MnSO_4$ solution.

From Eq. (2) the inverse manganese capture fraction may be given by

$$\frac{1}{f}=1+\frac{\sigma_S}{\sigma_{Mn}(1+G\bar{r}s)_{Mn}}+\frac{4\sigma_O}{\sigma_{Mn}(1+G\bar{r}s)_{Mn}}+\frac{N_H}{N_{Mn}}\cdot\frac{\sigma_H+0.05\sigma_O}{\sigma_{Mn}(1+G\bar{r}s)_{Mn}} \quad (3)$$

The term for oxygen can be omitted from this expression because σ_O is very small as 0.27 mb while σ_{Mn}, σ_H are 13.3b, 0.332b respectively and its effect is negligible.

$$\frac{1}{f}=1+\frac{\sigma_S}{\sigma_{Mn}(1+G\bar{r}s)_{Mn}}+\frac{N_H}{N_{Mn}}\times\frac{\sigma_H}{\sigma_{Mn}(1+G\bar{r}s)_{Mn}} \quad (4)$$

Eq. (1) may be rearranged as follows to form a straight line equation.

$$\frac{\varepsilon\cdot(1-L)\cdot(1-S)\cdot(1-0)}{A_S}=\frac{1}{Q}\times\left[1+\frac{\sigma_S}{\sigma_{Mn}(1+G\bar{r}s)_{Mn}}+\frac{N_H}{N_{Mn}}\times\frac{\sigma_H}{\sigma_{Mn}(1+G\bar{r}s)_{Mn}}\right] \quad (5)$$

The variation of $(1+G\bar{r}s)$ is only a few parts per thousand from published data[1]. Measurements are now carried out for a range of values of N_H/N_{Mn}, and the left-hand side of Eq. (5) can be plotted against $(N_H/N_{Mn})/(1+G\bar{r}s)_{Mn}$. A straight line is fitted to the data by a least squares method, and the intercept for zero N_H/N_{Mn} yields the quantity $\frac{1}{Q}\left[1+\frac{\sigma_S}{\sigma_{Mn}(1+G\bar{r}s)_{Mn}}\right]$ from which the source strength is obtained without reference to the σ_H/σ_{Mn} ratio. The slope of the line is $(1/Q)(\sigma_H/\sigma_{Mn})$. Therefore, the measurement

of the slope and the intercept yield not only the source strength, but also the effective cross-section ratio σ_H/σ_{Mn}. The ratio σ_H/σ_{Mn} determined by *K.* Kudo[3] is $0.02531 \pm 0.277\%$. However, the ratio of the individual cross sections taken from S,F, Mughabghab et al.[4] is $0.02501 \pm 1.52\%$.

The impurities can be allowed for conveniently by introducing the concept of an imaginary element Im of atomic weight A_{Im} which accounts for the weight of the impu rities during the determination of N_H/N_{Mn} by the gravimetric method. The neutron capture cross-section σ_{Im} is chosen to give the correct neutron aqsorption properties to the $MnSO_4$ solution from published data[4] as is the resonance activation integral parameter s_{Im}. The specification of the solution becomes[5]

$$MnSO_4+\left(\frac{N_{Im}}{N_{Mn}}\right)ImSO_4+\left(\frac{N_H}{2N_{Mn}}\right)H_2O.$$

The inverse manganese capture fraction becomes as the following form:

$$\frac{1}{f}=1+\frac{N_{Im}}{N_{Mn}}\cdot\frac{\sigma_{Im}}{\sigma_{Mn}}\cdot\frac{(1+\bar{r}s)_{Im}}{(1+G\bar{r}s)_{Mn}}+\left\{1+\frac{N_{Im}}{N_{Mn}}\right\}\times\frac{\sigma_S}{\sigma_{Mn}}\cdot\frac{(1+\bar{r}s)_S}{(1+G\bar{r}s)_{Mn}}+\frac{N_H}{N_{Mn}}\cdot\frac{\sigma_H}{\sigma_{Mn}}\cdot\frac{1}{(1+G\bar{r}s)_{Mn}} \quad (6)$$

Now the data are fitted to the expression of a straight line, $y=ax+b$. For a given concentration,

$$y=\frac{\varepsilon\cdot(1-L)\cdot(1-S)\cdot(1-0)}{A_s}$$

$$x=\frac{N_H}{N_{Mn}}\cdot\frac{1}{(1+G\bar{r}s)_{Mn}}$$

$$b=\frac{1}{Q}\left\{1+\frac{N_{Im}}{N_{Mn}}\cdot\frac{\sigma_{Im}}{\sigma_{Mn}}\cdot\frac{(1+\bar{r}s)_{Im}}{(1+G\bar{r}s)_{Mn}}+\left\{1+\frac{N_{Im}}{N_{Mn}}\right\}\frac{\sigma_S}{\sigma_{Mn}}\cdot\frac{(1+\bar{r}s)_S}{(1+G\bar{r}s)_{Mn}}\right\}$$

$$a=\frac{1}{Q}\cdot\frac{\sigma_H}{\sigma_{Mn}}\cdot$$

3. CHEMICAL ANALYSIS OF $MnSO_4 \cdot H_2O$

The chemical analysis of the $MnSO_4 \cdot H_2O$ from the Oriental Chemical Industry (OCI), was carried out by the inductively coupled plasmas (ICP) emission spectroscopy. This argon-supported ICP is an excellent excitation source for analytical atomic emission spectrosopy. The atomic excitation process is remarkably free of inter-elemental interactions. The technique whereby a solution is nebulized and blown into a high temperature ($\sim 6000°C$) plasma allows the determination of a great number of elements at all concentration levels.

The elements of impurities are given in Table 1. Column 3 of Table 1 shows the number of micrograms of each of fourteen elements, normalized to one gram of anhydrous $MnSO_4$. Column 4 shows the mass of impurity compound, usually the sulphate, present in the dry weight of the $MnSO_4$. The contribution is based on column 3. Columns 5, 6, and 7 show the individual calculated contributions to N_{Im}/N_{Mn}, $N_{Im}(g\sigma)_{Im}/N_{Mn}$, and $N_{Im}\sigma_{Im}s/N_{Mn}$ required for the analysis, where g is the Westcott factor which allows fos departure of σ_{Im} from the 1/v law. In the absence of resonance, the neutron capture cross section is inversely proportional to the neutron velocity, v. In order to obtain the correct sulphur contribution, column 5 actually represents the relative number of sulphate groups. For example, the contribution to N_{Im}/N_{Mn} from sodium is the number of units of Na_2, from magnesium is the number of units of Mg_1, and for aluminum it is the number of units of $Al_{2/3}$.

From the data of Table 1 the following information can be derived:

Table 1. Abundance of impurities in original $MnSO_4 \cdot H_2O$.

Z Number	Element	Impurity ppm of Element	Contribution ppm to dry weight $MnSO_4$	N_{Im} / $N_{Mn} \times 10^4$	$N_{Im}(g\sigma)_{Im}$ / $N_{Mn} \times 10^4$	$N_{Im}\ \sigma_{Im}\ S_{Im}$ / $N_{Mn} \times 10^4$
11	Na	150	463.6	5.03	5.28	0.81
12	Mg	3404	16856.6	213.9	13.49	2.34
13	Al	14	89	1.18	0.18	0.06
19	K	2650	5905.7	52.24	218.6	6.44
20	Ca	1383	4696	52.74	22.63	0.38
24	Cr	4	15	0.173	0.36	0.04
26	Fe	20	54	0.5	1.40	0.16
27	Co	1	154.7	1.58	59.14	105.2
28	Ni	72	189.9	1.85	8.26	0.43
29	Cu	13	32.5	0.312	1.157	0.52
30	Zn	2201	5421	50.54	56.25	105.2
48	Cd	9	16.8	0.122	397.7	194.2
3	Li	6	47.5	0.658	93.05	0
5	B	9*	29	0.635	964.8	0
	Total		33971.5	381.46	1842.3	415.78
25	Mn		966028.5	10000	133000	86800

* The value for B was obtained by the are emission spectroscopy.

$(g\sigma)_{Im} = 4.830$ b

$(s/g)_{Im} = 0.226$

$(s\sigma)_{Im} = 1.092$ b

$N_{Im}/N_{Mn} = 0.0381$

$N_{Im}\ \sigma_{Im}(g+\bar{r}s)_{Im}/N_{Mn}(1+G\bar{r}s)_{Mn} = 0.013735$

for $N_H/N_{Mn} = 100$ in $MnSO_4$ solution.

Therefore, the number of neutrons absorbed by the impurities listed in Table 1 is about 1.37% of the, neutrons absorbed by manganese, and it follows that this impurity data will result in an increase in an increase in the derived source strength

4. RESULT AND DISCUSSION

Allowance for the neutron absorption properties of the fourteen impurities affects the whole fitting procedure, and produces different values for both the neutron source strength and the manganese to hydrogen thermal neutron cross section ratio. The relevant impurities, mainly potassium, cobalt and zinc as well as small traces of cadmium, lithium, and boron absorb about 1.37% of the neutrons captured by manganse.

It is necessary to consides whether capture of neutrons in the impurities leads to measurable activity which would introduce a time dependent bias to the result. Assuming that no measurable activity is produced, the linearity of the fit should be unaffected if the impurity concentration is proportional either to that of manganese or to that of hydrogen.

Most of the elements with high neutron absorption, e.g., lithium boron, cobalt, and cadium may be assayed by conventional wet chemistry and instrumental analytical techniques.[6] However, a problem may exist for the assay of very low levels of gadolinium

of rare-earth elements. The presence of 1 ppm of gadolinium with respect to manganese, which has a thermal neutron cross section of 50,000 b in the relatively complex matrix of the manganous sulphate, would necessitate a correction of about 0.1% for neutron absorption[7].

5. CONCLUSION

The elements comprising Table 1 with hydrogen, Oxygen, manganese, and sulphur account for 18 of the natural elements. During the chemical analysis of $MnSO_4 \cdot H_2O$ samples no evidence was found to suggest that any of other 74 elements out of the 92 elements was present in the samples in the samples in a significant quantity. From the comparison of impurity levels in original $MnSO_4$ crystals it was learned that the chemical quality of $MnSO_4 \cdot H_2O$ from the OCI in KSRI was inferior to that used in NPL (National Physical Laboratory) for the neuron source strength measurements. As an example, the quantitative measurements are shown in Table 2 in comparison with the results obtained for the same three elements.

Table 2. Comparison of impurity levels in original $MnSO_4 \cdot H_2O$.

	ppm by weight of anhydrous $MnSO_4$	
Analyst	KSRI	NPL[5]
Mg	16857	7910
Na	464	609
Ca	4696	982
Sum	22017	9501

These results give strong confirmation to the view that the source of the impurities was the original supply of $MnSO_4$ crystals.

In addition, it is recommended to considerthat a search for rare-earth elements such as samarium, europium, and gadolinium with a rather high thermal neutron cross section should be made by the neutron activation analysis.

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망간용액조방법에 도입되는 국산 황산망간중의 불순물 분석

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=요 약=

중성자 선원의 강도를 측정하기 위하여 흔히 황산망간용액조 방법이 사용되고 있다. 본 연구에서는 $^{55}Mn(n,\gamma)^{56}Mn$ 반응에 도입되는 국산 $MnSO_4 \cdot H_2O$(동양화학제품)중에 불순물 성분을 규명하기 위하여 Ar-ICP 플라즈마방출 분광계측에 의한 분석화학 방법이 사용되었다.

분석결과로부터 주로 Co, Zn과 미량의 Cd, Li 등이 관련 불순물로서 중성자를 흡수하는 것으로 판명되었으며 전체 불순물에 의한 중성자 흡수 비율은 ^{55}Mn에 의하여 포획되는 중성자 수의 약 1.37%로 산정되었다.