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The Determination of the Most Appropriate Matrix Modifier for Tin Analysis by Electrothermal Atomic Absorption Method

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Abstract

In this study, the matrix modifier items given for tin in the literature have been determined, tin analyses have been made in the same conditions by using these substances, and by comparing the results, and optimum matrix modifier has been selected. The most appropriate concentration of the selected matrix modifier has been determined. It was seen that the most appropriate one among the 10 matrix modifiers specified in the studies in the literature was $Mg(NO_3)_2$, and that 4 - 5% concentrations of this substance were suitable concentrations for the ETAAS method. The results were compared by working with this matrix modifier on two standard reference materials and a commercial solder sample. The declared correct values of the reference materials and besides this, the results found with gravimetric and XRF have been accepted as correct values, and the results have been interpreted.

Keywords: Matrix modifier, Sn analysis, ETAAS method

1. Introduction

Many sources state that flame atomic absorption method (FAAS) can be used in the determination of the Cr, Mo and Sn elements with the atomic absorption spectrometry method. What's more, in the catalogs given by the atomic absorption device manufacturer companies together with the device, they declare designation boundaries which can be said to be quite low in the determination of these elements via FAAS method. However, in the applications in practice, these elements cannot be determined as easily via FAAS as it is said. These elements show fairly low absorbance values and the designation limits stated in these catalogs can never be reached. For example, the value specified for Sn in the catalog of many devices is generally between 1-140 mg/dm^3 (ppm) for FAAS, however even when working with pure standards within these limits, a reliable absorbance value cannot be reached. When you send a standard in a concentration of 1 mg/dm^3 Sn^{2+} to a flame in FAAS, it is not possible to read a noteworthy absorbance value. In the old literatures, the studies related to Sn(II) and Sn(IV) determinations in the direct FAAS applications are very limited, generally, the GFAAS studies made in the 1990s have been published, and in these studies, LOQ values for Sn have been given quite small besides matrix modifier (Elsheimer& Fries 1990, Pinel et al. 1986). In the recent studies, however, the LOQ values have been reported to be higher, and in the studies made with direct GFAAS method by using matrix modifier, higher LOQ values such as 3.2- 12.6 ng/g have been reported (Gholivand et al. 2008, Baysal et al. 2011, Knapek et al. 2009, Detsheva & Grobecker 2006). Small LOQ values such as 0.25 µg/L studied with GFAAS method have also been reported, but enrichment with ion exchanging resin has been made in the studies (Tsogas et al. 2009, Puri et al. 2004). In the food samples, there are also studies in literature with other analytical methods apart from the atomic spectroscopy methods on Sn analysis, and the LOQ values are also quite high in these studies, as well, and their Sn designations with UV-VIS spectrometry (Huang et al. 1997); and as fluorimetric (Morte et al. 2009) have been published. There are not many direct designations with FAAS in literature, and appointments over enrichment by using FAAS have been recently reported, and in these studies, enrichment has been made with Cloud Point Extraction (CPE) (Zhue et al. 2006, Ulusoy et al. 2012) In these studies, generally N_2O + C_2H_2 flame has been mostly used. For the electrothermal atomic absorption method (ETAAS), however, working range is given as 10-200 µg/dm^3 (ppb). But in reality, there is contradiction in these values, especially in limit of dedection (LOD) and limit of quantitation (LOQ) values. If the LOD and LOQ values are determined according to the blank solution (Armbruster et al. 1994, Skoog et al. 2007), a lower assignment value between 0.5- 2 µg/dm^3 is obtained, but a reliable absorbance value up to approximately 5-6 µg/dm^3 Sn^{2+} cannot be measured. The reason for this is probably the fact that these substances are transformed into their quite stable oxides (Cr_2O_3, MoO_2, SnO_2) in the flame environment, and that atomization due to the stability of these oxides is in a very small ratio. For this reason, these elements cannot be assigned easily with FAAS and only by using N_2O + C_2H_2 flame, assignment can be made in FAAS. It can even be said that it is impossible to assign them without the use of auxiliary substances. In this study, in the Sn analysis with FAAS and the electrothermal atomic absorption method, experimental studies have been conducted upon selecting the most appropriate matrix modifier required to be used in order to be able to make the assignment in a healthy way. The matrix modifiers given in the literature for this purpose have been designated, and the most appropriate of these and the optimum concentration has been determined. In the studies given in the literature over the past 30 years, different matrix modifiers have been used, $(NH_4)_2HPO_4$ (Mackie 1987) precious metals, especially Pd powder (Paudyn et al. 1988, Aucelio et al. 2000), picric acid and $K_2Cr_2O_7$ (Pinel et al. 1986), $Pd(NO_3)_2$ + $(NH_4)_2HPO_4$ mixture (Garcia et al. 2004), $Pd(NO_3)_2$ + $Mg(NO_3)_2$ mixture (Barrera et al. 1997), ascorbic acid (Zhue et al. 2006) and $Mg(NO_3)_2$ (Passias et al. 2012) have been suggested. In this study, a serial operation has been made in order to determine the one that shows the highest absorbance value of these substances given in the literature, and the results that were found have been compared with the Standard Reference Material (SRM) and the results of real examples. Study has been made with two SRMs, and after that, a commercially produced solder sample has been taken, and Sn analyses have been made by using the matrix modifier in the appropriate concentration. In the continuation of the study, SRM and the solder sample have been analyzed with classical gravimetric methods other than the AAS methods and with X-rays fluorescence (XRF) method and the Sn amount in their structures have been determined. Later, these values have been simply interpreted as statistics from the perspective of analytical chemistry.

In spite of the fact that Sn is not listed among the toxic elements, it is not listed among the essential elements, either, only their toxic effects on the living organisms has not been identified clearly (Kaim & Schwederski 2005).

2. Material and Method

The general issue that was observed in the experimental study is the fact that there is no absorbance value that can be taken to evaluation without using a matrix modifier both in FAAS and in ETAAS methods. It is inevitable to use a matrix modifier in order to be able to read the tangible absorbance values. Even when using a matrix modifier in the FAAS studies, the absorbance values could not be obtained higher than 0.30

value. In general, absorbance values lower than 0.1 have been observed in the FAAS method. In fact, this situation is surprising. Even in the qualitative analysis of Sn, many sources point to the luminescence experiment simply realized in a burner flame called flash experiment in the qualitative determination of Sn (Engelder 1947, Wilson & Wilson 1959**)**. Despite this, low absorbance values are observed in the standard Sn^{2+} solutions given to flame in atomic spectroscopy. Reliable absorbance values cannot be read without adding an environment regulator. As mentioned above, a lot of environment regulators have been given in literature, however, there are also contradictions in the applications of them, LOQ values very different from one another are declared in spite of the fact that study is performed with the same matrix modifier (Paudyn et al. 1988, Aucelio et al. 2000).

At this point, it is worth noting an issue. In spite of the fact that $(NH_4)_2HPO_4$, diammonium phosphate is recommended as an matrix modifier in many sources, no contribution of it as to the absorbance value of this material has been observed in our study, on the contrary, when there is Fe in the environment, adverse effects of diammonium phosphate have been encountered. In our study, when $Mg(NO_3)_2$, $MgSO_4$, $Sr(NO_3)_2$ substances of those given above are used as environment regulators, reliable absorbance values have been obtained. The highest absorbance values have been obtained with $Mg(NO_3)_2$ as expected. In the study, at first, study was made with FAAS, and $Mg(NO_3)_2$ in various ratios have been added to the standard solutions sprayed to the flame for this purpose. The matrix modifiers given above have been added to the environment in a way that will be 1, 2, 4, 5, 6 and 10 %. Due to the fact that the highest absorbance value is observed to be in the 4 % solutions, this concentration has been used as a standard in the ETAAS studies. This value is given as 2% in literature. In the values higher than 5 %, however, adverse effects have been observed in the absorbance. When $Na_2C_6H_6O_7$ $(NH_4)_2HPO_4$ and $Cd(NO_3)_2$ are used, almost no absorbance value has been read. In some literatures, $Mg(NO_3)_2 + (NH_4)_2HPO_4$ or $Pd(NO_3)_2 + Mg(NO_3)_2$ mixture is recommended (Garcia et al. 2004, Barrera et al. 1997), however, a superiority of this mixture over the single used $Mg(NO_3)_2$ has not been observed by us, on the contrary, the adverse effect of diammonium phosphate has been dominant. In the event that the oxidizing agents given above are used as environment regulators, too, a similar situation has been identified.

The atomic absorption device used in the study is GBC brand, Avanta PM Model spectrometer, 10.0 cm flame nozzle has been used, and in the ETAAS studies, however, injections have been made with the help of PAL 3000 auto sampler.

In the gravimetric designations, after the Bronze XXVI, Bronze XXXI and the solder sample were weighed in the analytical scale, it was dissolved in hydrothermal conditions by adding with 63 % certified HNO3 in a beaker, and it was heated for approximately for 2 hours after it was dissolved. SnO_2, which precipitates at the end of this period, has been filtered through G5 glass crucible and brought to a fixed weigh, and its Sn amounts have been calculated(Wilson & Wilson 1962, Harris 2007**)**. For ETAAS method, however, similarly a quantity of SRM and solder have been weighed, dissolved in a beaker by first using certified HNO_3, later, it was heated in a sand bath homogeneously, and it was evaporated until dryness. Then, by adding 5,0 cm^3 concentrated HCl and 5 cm^3 H_2O in a beaker, SnO_2 was made soluble, and by being diluted, it was used in an appropriate medium.

The other device that was used in the study was XRF device, and this device Spectro brand XLAB II Polarize XRF model. Three random points were selected and analysis was made, and average values were given.

In the study, first of all, standard Sn^{2+} %1, 2 in a concentration of 100 µg/dm^3 was prepared in $Mg(NO_3)_2$ of 4, 5, 6 and 10 in a concentration that was stated before, and it was sprayed to the flame, and the magnitude of its absorbance value was measured. After many repetitions, it was observed that its absorbance value was in the highest level between 2 - 4 %, that the absorbance did not increase more as $Mg(NO_3)_2$ concentrated. When worked with all the other environment regulators in a similar way, it was seen that its absorbance value was not affected much, **Table 1**. For this reason, when working with graphite tubs, only matrix modifier in which absorbance value increased was used. In **Table 1**, the FAAS and ETAAS working conditions were also given.

Table 1 The absorbance values with respect to the dependence of the 100 μg/dm^3 Sn^{2+} solution to the matrix modifier concentration of the absorbance value.

Method	Concentration of the $Mg(NO_3)_2$ (%)	Observed Absorbance range	Working conditions and thermal program
FAAS	1	0.003-0.011	λ=235.50 nm Slit width: 0.5 nm Read time: 3 s n:3 Background correction: D_2 Acetylene flow rate:1.49 dm^3/min. Air flow rate: 10.00 dm^3/min.
	2	0.02-0.03	
	4	0.025-0.050	
	5	0.023-0.049	
	6	0.018-0.049	
	10	0.02-0.051	
ETAAS	1	0.04-0.11	λ=235.50 nm Slit width: 0.5 nm Read time: 3 s n:3 Background correction: D_2 Argon flow rate: 6.0 dm^3/min. GF program: First drying:80 °C , Hold time:20 s Second drying: 120 °C , Hold time 20 s, Ramp time:10 s Ashing :400°C, Hold time 10 s, Ramp time: 5 s Atomization: 2400 °C, Ramp time:1.5 s, Read time: 1.2 s Cleaning :2500 °C, 1 s
	2	0.18-0.34	
	4	0.38-0.56	
	5	0.36-0.55	
	6	0.34-0.55	
	10	0.33-0.59	

By using $Mg(NO_3)_2$ of 4 %, one of the calibration curves obtained with 10-100 μg/dm^3 standard solutions is seen in **Figure 1**. In **Figure 1a**, an example of the calibration curves obtained with FAAS in the above conditions, in **Figure 1b**, however, a sample calibration curve obtained with ETAAS is seen. As a requirement of analytical study, the effect of the destructive ions was examined and 6 metals that can match with Sn were determined. These metals were determined as Cr, Fe, Ni, Cu, Zn, Cd, and Pb. In this determination, the elements that can alloy with Sn were chosen. Solutions in a concentration of 100 times more of the Sn concentration were prepared and their calibration curves were repeated, however, it was detected that none of these elements had an enterprise effect, **Figure 2**.

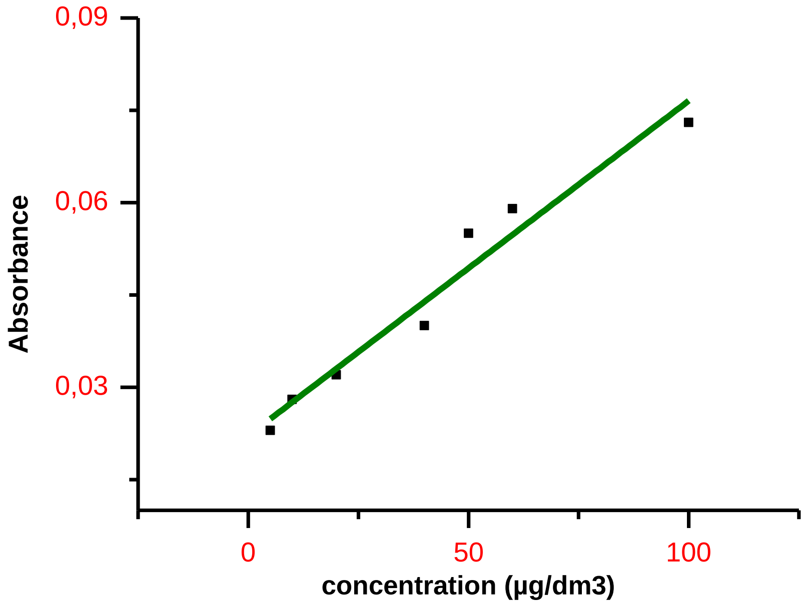

Figure 1a. The calibration curve obtained with FAAS in a 10-100 µg/dm^3 Sn^{2+} concentration range , matrix modifier concentration = % 4.

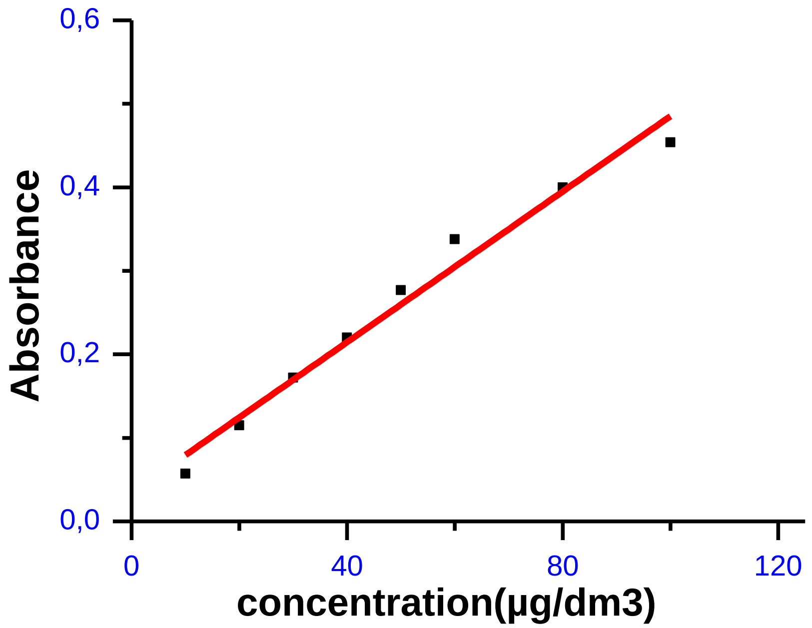

Figure 1b. An example of the calibrations obtained with ETAAS besides 4 % Mg(NO$_3$)$_2$ matrix modifier. It is seen that the absorbance value is higher compared to the FAAS method.

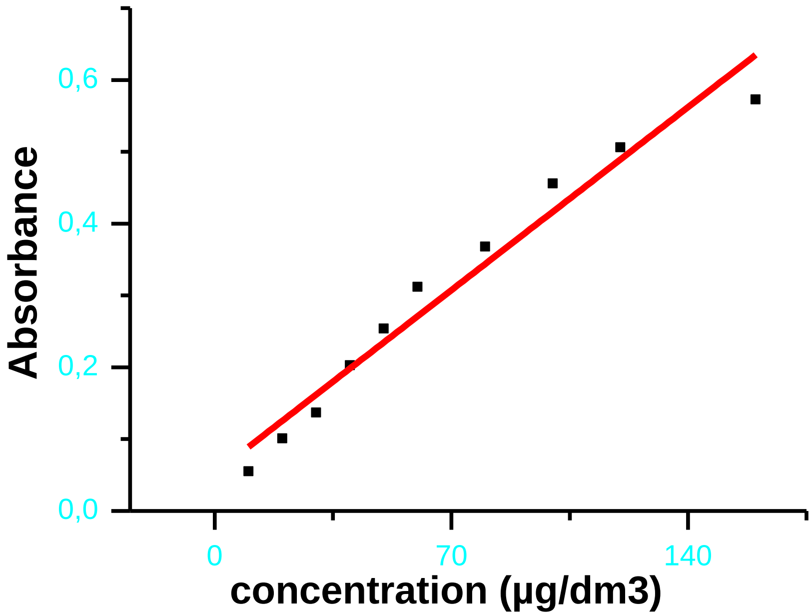

Figure 2. The calibration curve obtained with 10-100 µg/dm^3 Sn^{2+} solutions besides 10 mg/dm^3 Fe^{3+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}.

It is almost the same as the calibration curve obtained without matrix items.

The lower limit of determination is generally found by reading many absorbance values of the witness solution, and calculating the standard deviation and multiplying by a certain coefficient. However, this method is not very meaningful in the designation of Sn. In spite of the fact that a clear absorbance cannot be read in the concentrations lower than 10 µg/dm3, the LOQ value is calculated around some µg/dm^3 with this method. For this reason, in order to be able to monitor the lower limit of determination in the study, a calibration graph was prepared with solutions in a concentration of 1-50 µg/dm^3, and LOQ value was estimated by looking at this chart, **Figure 3**. Generally, a great number of witness solutions are forwarded to the device in the determination of the lower limit, and the standard deviation of the values read by the device is determined, and the values that are 3 times greater than this value are considered as signals that belong to the analyte (Armbruster et al. 1994, Skoog et al. 2007). The signals that are 10 times the value of this standard deviation are considered as LOQ value. However, the lower determination limits designated with this method are not very meaningful in the Sn analysis, because, the software of the devices already calculates these standard deviations. If LOQ values are calculated according to these standard deviations, approximately 0.9-1.5 µg/dm^3 LOQ value is found in this study. However, when the absorbances of the Sn^{2+} solutions are read in these concentrations, almost the same absorbance as the witness absorbance are read. If **Figure 3** is examined carefully, 0.005 absorbance value is read even in 2.5 µg/dm^3 concentration, and this part of the calibration curve is typically S-shaped. If the region where the absorbance is increased in a linear position is taken into consideration, the LOQ value in this study is between 5-10 µg/dm^3.

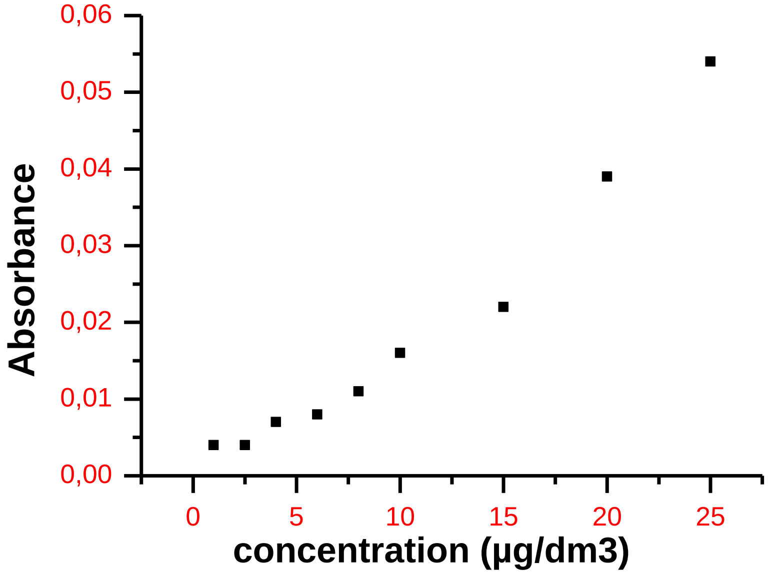

Figure 3. In order to be able to see the lower limit of determination, the calibration curve that has been obtained with Sn^{2+} solutions in a range of 2.5-25 µg/dm^3.
If attention is paid, it can be seen that LOQ value is between 5-10 µg/dm^3.

After that, certified two standard alloy examples were selected and the Sn amounts in these alloys were analyzed first with the classic gravimetric method, then with XRF method, and after that, with ETAAS. The biggest challenge for ETAAS is the multitude of the number of dilutions. After that, a commercially produced solder sample was procured in the study, and the same processes were also applied to the solder sample. In **Table 2**, the declared and found Sn values of the SRM two alloys and the solder sample have been given.

Table 2 In the SRM and solder samples, the results found with ETAAS, XRF and gravimetric methods

Material	Sn Value in Certified SRM (%)	Value found by gravimetry (%)	Value found by XRF (%)	Value found by ETAAS (%)
Bronze XXVI	10.04	9.67±0.16	9.81	9.54±0.63
Bronze XXXII	12.71	12.15±0.79	10.98	11.07±0.76
Solder		41.98±.60	38.81	40.15±0.95

Is there a difference between the results? With the eyes of an analysis maker, there are 3 correct values if we assess statistically, certified values, gravimetric results and XRF results. For this reason, a statistical comparison is not given here. But, the proximity of all the values to one another is seen clearly. Of the results found above, if the ones obtained with gravimetry and ETAAS made by us are given in a 95 % confidence interval together with the analysis number, the following values appear, **Table 3**.

Table 3 The relative errors of the results found and their values in a 95 % confidence interval

Material	Value found by gravimetry	Value found by ETAAS	The relative errors (%) according to certified value	The relative errors (%) according to gravimetry value	The relative errors (%) according to XRF value
Bronze XXVI	9.67±.18 N=5	9.54±0.61 N=7	6.29	1.36	2.72
Bronze XXXII	12.15±0.90 N=5	11.07±0.74 N=7	14.81	9.76	0.8
Solder	41.98±0.69 N=5	40.15±1.09 N=5	--	4.55	3.33

As it is seen **Table 3**, if the certificate value given for bronze XXXII is correct, the relative error only found for this item is high (14.81 %). If gravimetry is taken into consideration, the relative errors are below 10 %.

3. Results and Discussion

Sn is one of the elements whose analysis is quite difficult in atomic absorption. FAAS almost does not give any absorbance value. Only when an matrix modifier is added, positive absorbance is observed. It is detected that in the study, the most appropriate matrix modifier is the 4 % Mg $(NO_3)_2$ environment. In higher concentrations, the study did not make a contribution. A positive effect of diammonium phosphate, which is highly recommended in literature, is not encountered, and it was also detected that it created a problem with the matrix attendantly. Its effect to the precision of the study was not observed in the environment regulators recommended as an oxidizing agent. Reliable absorbance values were obtained only with Mg $(NO_3)_2$. Even if we work with this regulator, it is inevitable to work with ETAAS so that the analytical precision is high, and the values obtained at FAAS are not reliable absorbance values. % recovery was spread between 87.75 and 105.73. In the study, a solder sample obtained from the market was also analyzed and for the solder, first of all, analysis was made in a semi micro-level as the gravimetric in order to determine the Sn amount in it, and as a result of this, it was detected that there was 41.98±1.56% Sn in the solder. This value was accepted as the correct value, and the % recovery was found as 95.64±3.41 in the analysis of the solder with ETAAS in a similar way.

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