



Influence of sample pan on the thermal behaviour of KSCN measured with TG

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Abstract

In this study, the influence of the sample pan on the thermal behaviour of potassium thiocyanate (KSCN) was investigated. The measurements were performed with thermogravimetry (TG) and the two sample pans used were a platinum pan and a ceramic crucible. The samples were heated to 400–950 °C and the thermal products were identified by powder diffraction.

The thermal behaviour of KSCN was found to be dependent on the sample pan used. With the platinum sample pan KSCN reacted in the first step into a mixture of K_2SO_4 and potassium tetracyanoplatinate ($K_2Pt(CN)_4$). In the second step, the mixture reacted further to pure K_2SO_4 . In the ceramic sample crucible, however, the reaction in the first step resulted in a mixture of K_2SO_4 and KOCN. In the second step, the mixture reacted further to pure K_2SO_4 .

The results were verified with additional measurements of rubidium thiocyanate (RbSCN) and cesium thiocyanate (CsSCN). The reactions of these compounds proved to be similar to those of KSCN, thereby confirming that the thermal behaviour of the alkali metal thiocyanates mentioned in this study, depends on the sample pan used.

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1. Introduction

The thermal decomposition of alkali metal thiocyanates has been studied previously [1,2]. According to these studies, the thiocyanates decompose through oxidation to sulphates, e.g. potassium thiocyanate (KSCN) oxidises without intermediates into K_2SO_4 upon heating. Nonetheless, in this study the thermal behaviour of KSCN was found to be more complex. The percentage weight of the intermediate in the thermo-analytical curve failed to correspond to the calculated percentage weight of K_2SO_4 formed in

the oxidation of KSCN. The thermo-analytical curves of KSCN are shown in Fig. 1.

The aim of this study is to prove that instead of oxidising straight into K_2SO_4 , KSCN reacts in the first step to form a mixture containing K_2SO_4 and another potassium compound. In the second step, the mixture reacts further into pure K_2SO_4 . The composition of the potassium compound in the first intermediate depends on the sample pan used in the thermogravimetry (TG) measurement. When measured in a platinum pan, KSCN reacts in such a way that a mixture of K_2SO_4 and $K_2Pt(CN)_4$ is formed. When measured in a ceramic crucible, KSCN reacts to form a mixture of K_2SO_4 and KOCN. Thermal behaviour was determined by thermogravimetry (TG) and the intermediates were identified by X-ray powder diffraction.

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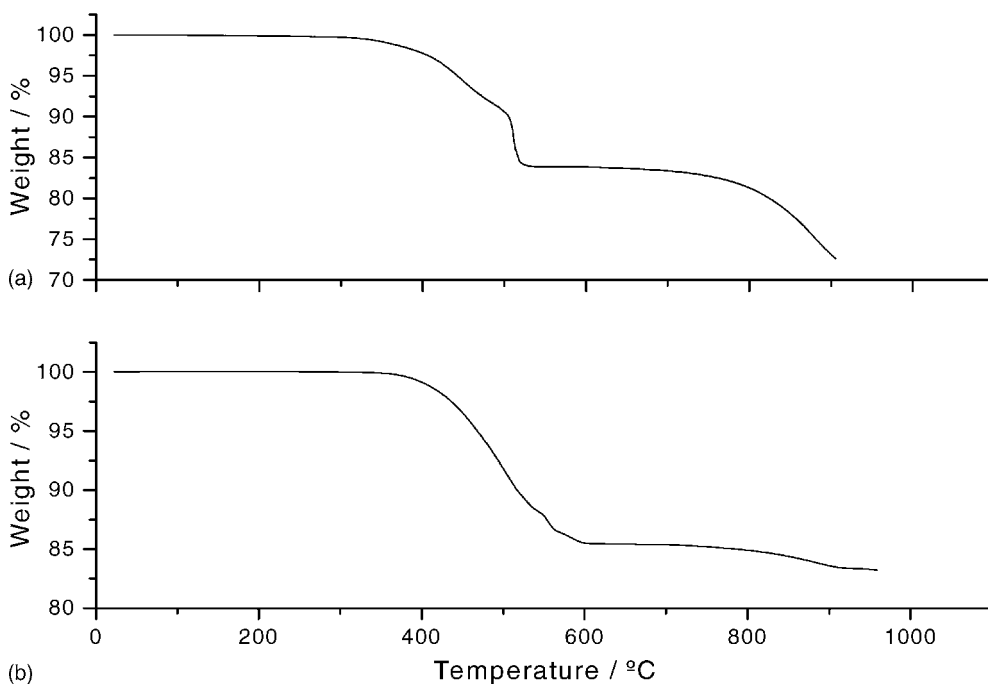


Fig. 1. Thermo-analytical curve of KSCN measured (a) in the platinum pan and (b) in the ceramic crucible.

2. Experimental

2.1. Materials

The majority of the measurements in this study were done with potassium thiocyanate (KSCN). Some comparative measurements were done with rubidium thiocyanate (RbSCN) and cesium thiocyanate (CsSCN). KSCN was provided by Fluka. RbSCN and CsSCN were prepared by dissolving their carbonates in aquatic solution of ammonium thiocyanate, NH_4SCN . NH_4SCN (Aldrich) was dissolved in water and an equivalent amount of Rb_2CO_3 (Aldrich) or Cs_2CO_3 (Aldrich) was added to the solution. The thiocyanates were crystallized at room temperature.

2.2. Instrumentation and procedure

The thermal decomposition measurements were performed using a Perkin-Elmer TGA 7 Thermogravimetric Analyzer. The sample pan was either a platinum sample pan and a stirrup (Perkin-Elmer part nos.

0319-0264 and 0319-0265) or a ceramic (alumina, Al_2O_3) crucible (Perkin-Elmer part no. N5370464). The amount of the sample was 5–10 mg, the heating rate was 2°C min^{-1} and the temperature range was 22–950 °C. The samples were studied under a synthetic air atmosphere with a flow rate of 50 ml min^{-1} .

KSCN was finely ground and placed into the sample pan. The sample was heated to 950 °C to observe the entire thermal decomposition curve. To solve the composition of the intermediates, KSCN was heated several times to both 470 and 600 °C and the residues were recovered. The compositions of the residues were characterized by powder diffraction.

The powder diffraction patterns were obtained at room temperature using a Huber Imaging Plate Guinier Camera G670. Programs G670 (version 3.2.17) and Bede ZDS (version 4.21) were used to collect and process the measurement data, respectively. The measured powder patterns were identified with the PDF-2 database of known powder diffraction patterns. The X-ray source was monochromatised $\text{Cu K}\alpha_1$ radiation and the X-ray tube was operated at 40 kV and 25 mA. The measuring time was 30 min

and the diffraction angle was $0^\circ < 2\theta < 100^\circ$. The samples were well mixed and ground in advance as in the TG measurements.

3. Results and discussion

3.1. Pt pan

The thermal behaviour of KSCN was first measured in the platinum pan. Numerous measurements were made but the thermo-analytical curve differed systematically from the reaction route suggested by a previous study: $2\text{KSCN}(\text{s}) + 5\text{O}_2(\text{g}) \rightarrow \text{K}_2\text{SO}_4(\text{s}) + \text{SO}_2(\text{g}) + 2\text{CO}_2(\text{g}) + \text{N}_2(\text{g})$ [2]. According to the same study, the percentage weight of the sample at 600°C is 89.6%. However, in our measurements the percentage weight at 600°C was about 83.8%. The measured TG curve is shown in (Fig. 1a). The relatively stable intermediate at $500\text{--}700^\circ\text{C}$ was identified by powder diffraction. First, KSCN was measured several times to 600°C with the TG and after every measurement the residue was recovered. When enough of the residue

had been obtained, its powder diffraction pattern was measured. The powder pattern is shown in (Fig. 2a). The residue was identified as a mixture of K_2SO_4 and Pt. The platinum originated from the sample pan and thus it was ignored in the reaction calculations. Despite the fact that the intermediate was found to be potassium sulphate, the percentage weight of the intermediate was not in accordance with the idea, previously suggested [1,2], that KSCN decomposes straight to K_2SO_4 .

Additional measurements included heating KSCN several times to about 450°C and collecting the residues for powder diffraction identification. The powder pattern obtained is shown in (Fig. 2b). The results were somewhat surprising. Most of the residue seemed to be K_2SO_4 , but on this occasion another compound was also present. This compound was identified as potassium tetracyanoplatinate ($\text{K}_2\text{Pt}(\text{CN})_4$). Apparently, KSCN reacted with the platinum sample pan to form $\text{K}_2\text{Pt}(\text{CN})_4$.

However, between 450 and 600°C $\text{K}_2\text{Pt}(\text{CN})_4$ reacted leaving pure K_2SO_4 and elemental Pt. The thermal decomposition of $\text{K}_2\text{Pt}(\text{CN})_4$ has been solved by

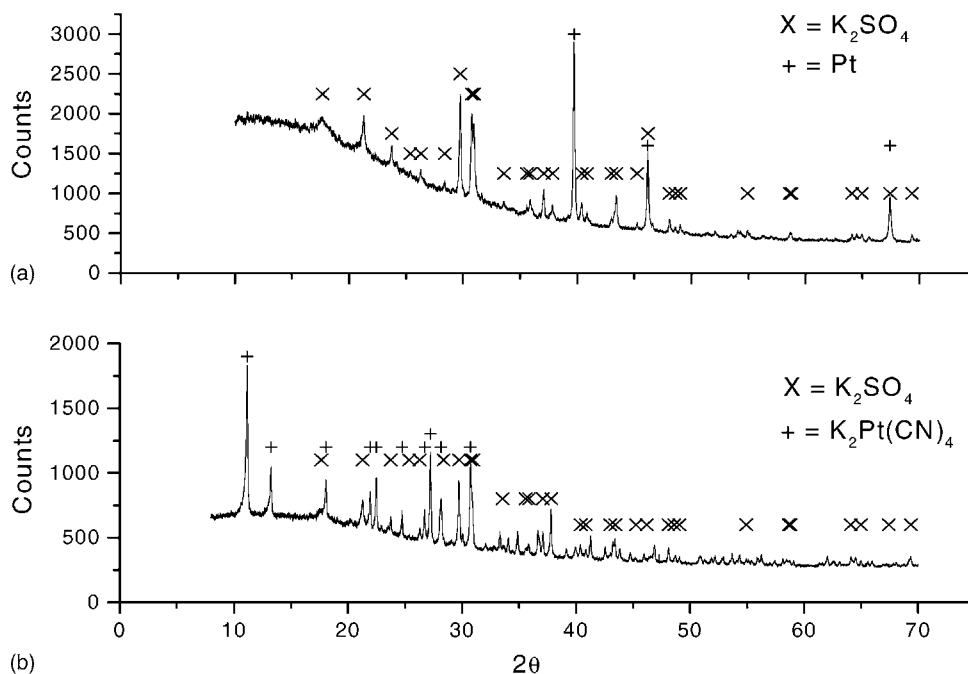
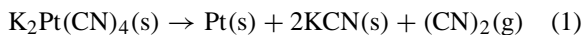
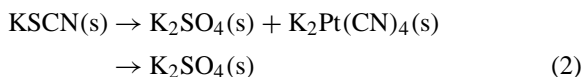


Fig. 2. Powder diffraction pattern of (a) the second intermediate at 600°C and (b) the first intermediate at 470°C . KSCN was measured in the platinum pan.

Gallagher and Luongo [3]:



The elemental platinum formed in the decomposition of $\text{K}_2\text{Pt}(\text{CN})_4$ remained in the pan as it appeared in the powder diffraction pattern taken from the second intermediate (Fig. 2a). The $(\text{CN})_2$ vanished into the controlled atmosphere. Although solid KCN was formed, it was no longer present in the second intermediate collected at 600 °C. A satisfactory explanation, yielded by previous studies, is that KCN sublimes without decomposition around 500–600 °C [4–6]. To sum up the findings, it can be suggested that KSCN reacts when heated to 950 °C, according to the following reaction scheme:



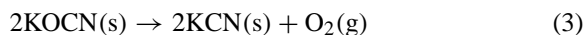
Because $\text{K}_2\text{Pt}(\text{CN})_4$ decomposes according to reaction 1, part of potassium is lost as KCN sublimes around 500–600 °C [4–6]. That explains why the percentage weight of the stable intermediate at 500–700 °C is lower in this study than it was in the previous study [2]. In this study, the compositions of the gaseous reaction products could not be identified precisely. Thus, the exact balanced stoichiometric equations can not be used. However, the solid intermediates were identified with certainty by powder diffraction.

3.2. Al_2O_3 crucible

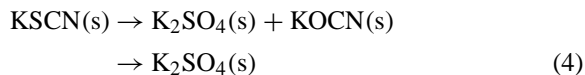
The sample pan was changed to a ceramic crucible made of aluminium oxide (Al_2O_3). The purpose was to prove that the unexpected behaviour of KSCN upon heating was related only to the Pt pans. The oxidation of KSCN when the ceramic crucible was used was expected to follow the reaction route suggested in the previous study [2]. Despite this assumption, the TG curve or the percentage weights of the intermediates were not in accordance with the theoretical reaction route in this case either. The thermo-analytical curve measured with TG is shown in (Fig. 1b).

Again KSCN was heated to both 510 and 650 °C several times and the residues were collected and identified by powder diffraction. Also, with the ceramic crucible the relatively stable second intermedi-

ate at 600–800 °C was found to be pure K_2SO_4 , as seen in (Fig. 3a). The difference is once again observed in the first intermediate at 510 °C. As shown in (Fig. 3b), it was identified as a mixture of K_2SO_4 and KOCN. Thus, the thermal behaviour of KSCN measured in the ceramic crucible differs from that measured in the Pt pan and also follows a different route from that found in the previous study [2]. The thermal decomposition of KOCN has been studied and the decomposition route suggested to be following [6,7]:



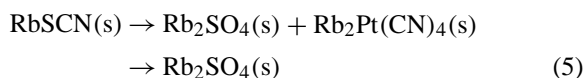
The thermal behaviour of KSCN, when measured in the ceramic crucible, follows the reaction scheme:



Part of potassium is lost as KCN in this reaction also, because KOCN decomposes according to reaction 3 and the KCN sublimes around 500–600 °C [4–6].

3.3. RbSCN and CsSCN

The thermal behaviour of RbSCN and CsSCN was measured in the platinum pan and in the ceramic crucible to confirm the results obtained with KSCN. With both compounds the measurements followed the results obtained with KSCN. The TG curves of RbSCN are shown in Fig. 4, CsSCN behaved similarly. With the Pt pan the first intermediates at about 510 °C were not perfectly identified. As seen in (Fig. 5a), there are peaks of Rb_2SO_4 and also some additional peaks seen in the powder diffraction pattern. The additional peaks could not be identified as platinum compounds similar to $\text{K}_2\text{Pt}(\text{CN})_4$, as the database PDF-2 does not yet recognise either $\text{Rb}_2\text{Pt}(\text{CN})_4$ or $\text{Cs}_2\text{Pt}(\text{CN})_4$. Nevertheless, the peaks were not identified as any other compound either. The second intermediate at 650 °C was recognised as a pure sulphate of the alkali metal measured, Rb_2SO_4 or Cs_2SO_4 . So, it is relatively safe to assume that these compounds decompose similarly to KSCN when heated in a Pt pan.



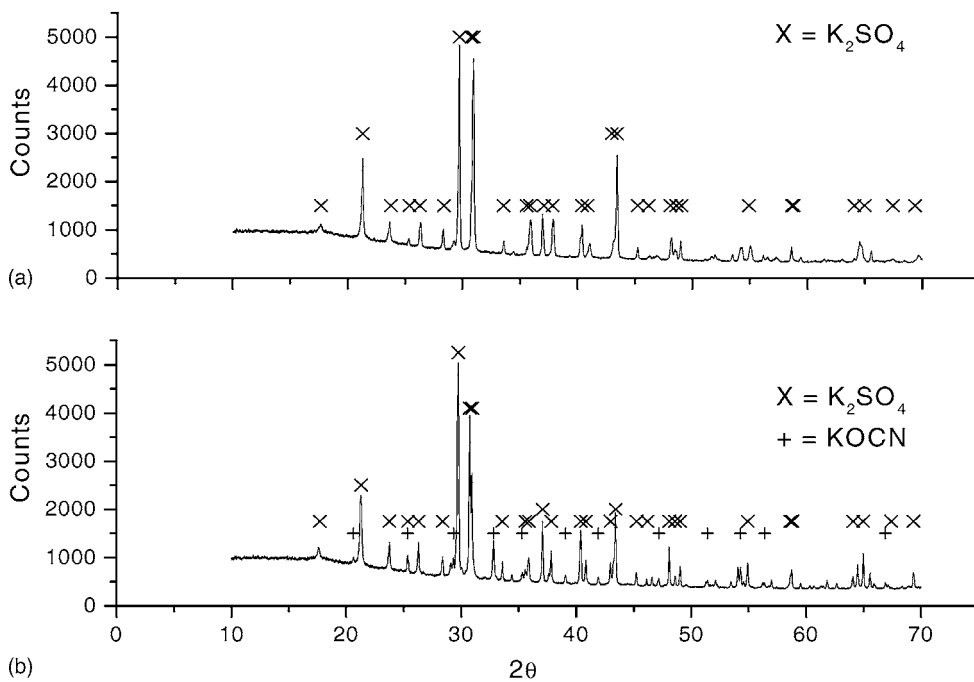


Fig. 3. Powder diffraction pattern of (a) the second intermediate at 600°C and (b) the first intermediate at 550°C. KSCN was measured in the ceramic crucible.

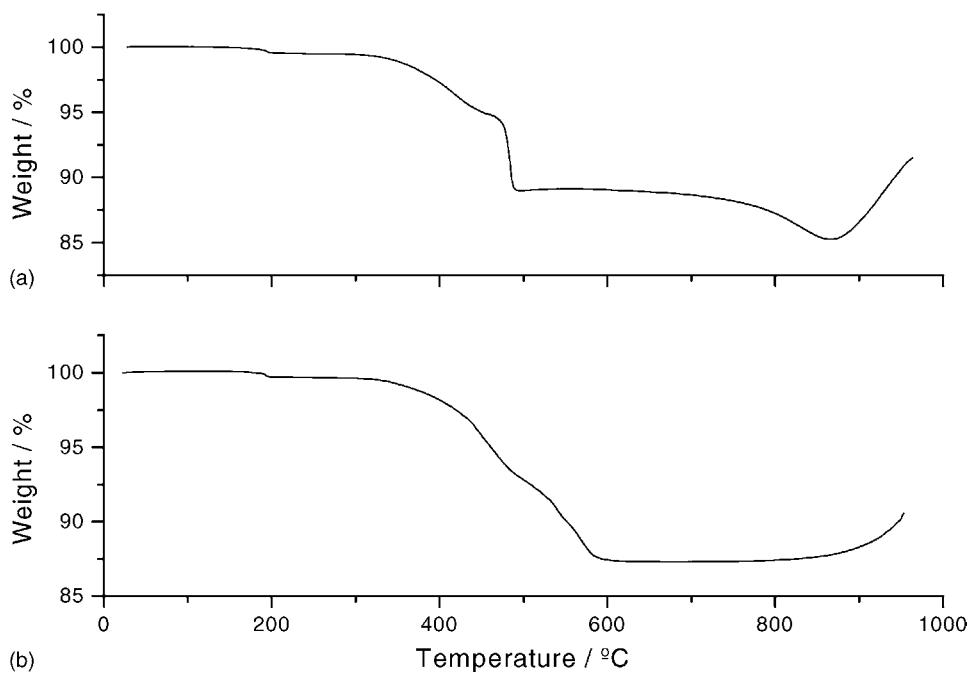


Fig. 4. Thermo-analytical curve of RbSCN measured (a) in the platinum pan and (b) in the ceramic crucible.

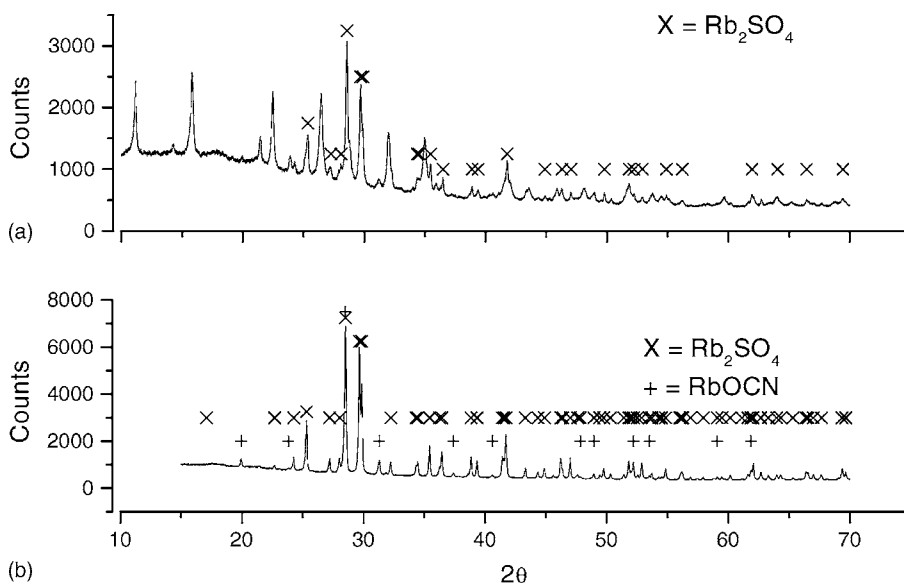
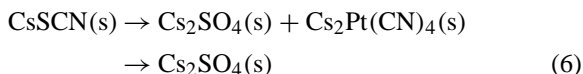
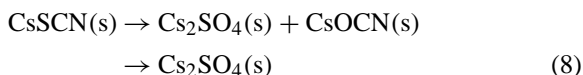
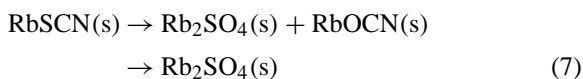


Fig. 5. Powder diffraction patterns of the first intermediates. RbSCN was measured (a) in the platinum pan and (b) in the ceramic crucible.



When RbSCN and CsSCN were heated in a ceramic crucible the results were identical to the results of KSCN. The first intermediates were mixtures of Rb_2SO_4 and RbOCN or Cs_2SO_4 and CsOCN, respectively. The second intermediates were pure sulphates, Rb_2SO_4 or Cs_2SO_4 . The powder diffraction pattern of the first intermediates of RbSCN is shown in Fig. 5b. Thus, the thermal decomposition of RbSCN and CsSCN in a ceramic crucible follow the reactions:



3.4. Discussion

It is observed in this study that the sample pan does affect the thermal behaviour of KSCN in TG measurements. Both pan materials used in this study, Pt and Al_2O_3 , seem to act as catalysts in the oxidation

of KSCN to K_2SO_4 . However, since platinum takes part in the actual reaction and forms a relatively stable compound, $\text{K}_2\text{Pt(CN)}_4$, it might be more accurate to state it as an activating material.

The reaction of KSCN was slightly different depending on which sample pan it was measured in. With the platinum pan the first step of the reaction starts earlier and it is faster. Especially, the last part of step one is extremely rapid as seen in (Fig. 1a) (about 500°C). After step one, a relatively stable intermediate is formed which starts to lose weight again after about 700°C . With the Al_2O_3 pan, the first reaction step starts later and the reaction itself seems to be steadier. The relatively stable intermediate reacts further but the weight loss in this case is only minor.

Although, we discovered that there is a connection between the reaction rate of KSCN and the sample pan materials used in this study, there are still many things that need to be studied further. Does the connection apply only to the two materials used in this study? When KSCN is measured in the platinum pan the weight of the relatively stable intermediate continues to fall after about 700°C . However, in the ceramic crucible the intermediate is more stable. Is the overall reaction already finished or will the second step of the reaction start later?

4. Conclusion

The results obtained in this study provide convincing evidence that the thermal behaviour of some alkali metal thiocyanates differ depending on the sample pan used in measurements. Most of the measurements were done with KSCN either in a platinum sample pan or in a ceramic sample crucible. In the platinum pan, KSCN reacts upon heating into a mixture of K_2SO_4 and $K_2Pt(CN)_4$ and further into pure K_2SO_4 . The intermediates were identified by powder diffraction. In the case of the ceramic crucible the first intermediate is a mixture of K_2SO_4 and KOCN, which reacts further into pure K_2SO_4 .

The unexpected results were confirmed by additional measurements of RbSCN and CsSCN. Both RbSCN and CsSCN behaved similarly upon heating both in the platinum pan and in the ceramic crucible. It

can be concluded that the thermal behaviour of these alkali metal thiocyanates depends on the sample pan used.

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