

Thermogravimetric Determination of Metals in Compounds containing Organometal and Metal by the Ashing Method

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Thermogravimetric determination of sulfate ash was studied. The equipment was improved to carry out an accurate analysis of TG: a pan stop and a tare with the same weights as the sample container was used to eliminate hysteresis in the balance, an insulator was placed at the junction between furnace and balance, and warm water was circulated to the casing, and was protected with the magnetic shield of the balance case. Thus baseline variation was reduced to less than 20 μg when the sample was heated up to 800°C. For the analysis, samples that were either hygroscopic or volatile were covered with a piece of cellophane tape and affixed securely to the interior wall of the sample container, thus sealing the sample. After the weight of container was adjusted to zero, a drop of sulfuric acid was added, the sample was heated, and the ash was weighed. The method thus permits accurate measurement of ash such as aluminum oxide, which is highly hygroscopic or its sample is either hygroscopic or volatile. With this method each measurement takes about one hour to obtain. The results are accurate and precise to a maximum error of 0.3% (2σ).

1. Introduction

Expanding applications of organometallic and metal-containing compounds across the spectrum of science and technology have given rise to the need for simple and yet accurate methods of performing quantitative analyses of their metallic constituents. The conventional method involves the wet ashing process followed by photometric analysis, using either conventional absorption spectrometry or atomic absorption spectrometry. This conventional method, however, takes a long time to decompose the sample

and does not generally yield accurate results. A dry ashing method, by contrast, is less cumbersome to use and is much faster. The dry ashing method is the best technique when a kind of a chemical species of the metal in the sample is known. Adding sulfuric acid during the ashing process, as widely used, promotes the capture of metal constituents in the sample as a sulfate and thus improves the accuracy of quantitative determination¹⁾.

The following describes methods of performing an accurate quantitative analysis of metals present in organometallic compounds by the sulfated ashing method based on thermogravimetry (TG). The conventional micro-muffle tube or crucible method fails to yield accurate weight determinations when the generated ash is hygroscopic²⁾. In contrast with the conventional methods, TG allows the worker to

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take weight measurements at high temperatures without being affected by the hygroscopic nature of the ash. For this reason, TG is able to be adopted as the gravimetric determination of aluminum and silicon. Another advantage of the TG method is that the heating conditions are able to be adequately controlled for preventing the sample from boiling over or undergoing rapid combustion during the ashing process. This also prevents vaporization of the generated ash through the application of excessive heat. Although TG has been improved to achieve accurate temperature measurements³⁾, it is not sufficiently accurate for making weight measurements to yield stoichiometrically meaningful results. The operation of a micro-balance involves problems as ventilation and heating, for obtaining accurate measurements. This report examines the modification of the TG equipment and establishing the proper method for eliminating sources of weighing errors, including rest-point shifting and variability in weighed values. The results have been equipment enhancements, improved determination procedures, and highly reliable measurement values. A method was also devised for performing accurate gravimetric determinations on samples that are difficult to weigh because they were liable to gain or lose water rapidly, thus a technique was developed for obtaining highly reliable measurements. The new method was used for quantitative analyses of various metals by sulfate ashing. The results were highly accurate, with a maximum error of 0.3%(2 σ). Under the new method a sample can be analyzed in less than one hour.

2. Experiment

2.1 Equipment and Reagents

For thermogravimetry, a PTC-10 thermal analysis station and a thermogravimetric analyzer (standard type) from Rigaku Co. were used with the following modifications.

A pan stop was attached to the magnetic damper. A heat insulating material was inserted between the aluminum block housing the TG balance and the cooling device for the sample-heating furnace. The housing unit was covered with both heat insulation and magnetic-shielding materials. A

PVC heat-retaining bag was attached to the bottom of the aluminum block. Cooling water for the balance was allowed to circulate in the PVC bag. The cooling water was put into a 40-liter tank, heated to 30°C by an immersible heater, and circulated through the PVC bag. A tare, approximately the same weight as the sample container, was used to ensure that the balance was always at equilibrium and undisturbed by large fluctuations.

A platinum sample container was used. The top of the sample container was folded inward to prevent the sample from boiling over⁴⁾. A M5S/A chemical micro-balance made by Mettler Corporation was used to weigh samples.

Standard atomic absorption spectrometry samples and special-grade JIS reagents were used as analytical samples listed in Table 1. Analytical data sheets supplied by the manufacturers of these samples were used for reference. The strength of the sulfuric acid added to the samples was 80 v/v%.

2.2 Analysis Procedures

The TG equipment was allowed to warm up prior to the analysis. Measurements were taken after a stable baseline was achieved, and were made as rapidly as possible to reduce TG equipment.

Approximately 10 mg of a sample were accurately weighed on the micro-balance. Samples that were likely to undergo weight changes due to moisture absorption during the weighing process were handled as follows: approximately 10 mg of the sample were placed in a previously weighed sample container (5 mm ϕ). The sample was covered with a weighed strip of cellophane tape (8 mm ϕ), with the adhesive side facing downward. A stainless steel rod with an outer diameter of 4 mm was used to press the sample onto the bottom of the container. Any outer edge of the piece of tape which was not in contact with the sample was affixed to the inner wall of the sample container, thus sealing the sample. The whole body was weighed. The difference between this weight and the sum of the weights of the container and the strip of tape was the weight of the sample.

The TG heating furnace was opened carefully. A wind-shielding cover was attached to the furnace.

Table 1 chemicals list used.

| | | |
|---------------------------------------|----------------------------------|----------------------------------|
| Aluminum acetylacetonate | Aldrich Chemical Company | Atomic absorption standard |
| Aluminum 3-acetylglucyrrerate | Ditto | Ditto |
| Aluminum 2-ethylhexanoate | Kodak | Ditto |
| Barium cyclohexanebutylate | Ditto | Ditto |
| Aluminum cyclohexanebutylate | Merck | Ditto |
| Iron (III) tris (phenyl butandionate) | Ditto | Ditto |
| Octaphenylcyclotetrasiloxane | Kishida Chemical Co.,Ltd. | Organic microanalytical standard |
| Sodium tartrate | Ditto | Ditto |
| Magnesium acetylacetonate | Ditto | Ditto |
| Iron (III) acetylacetonate | Ditto | Ditto |
| Aluminum formacetonate | Tokyo chemical Industry Co.,Ltd. | Ditto |
| Sucrafate | Chugai Pharmaceutical Co.,Ltd. | Official drug |
| Aspirin Aluminum | Daiwa Pharmaceutical Co.,Ltd | Ditto |
| Others | Kanto Chemical Co.,Ltd. | Special class or equivalent |

The sample container was placed on the sample pan holder. The equipment was adjusted for zero setting. One drop of sulfuric acid was added. The furnace was closed carefully to commence the ashing process. To prevent boiling over or too rapid combustion, the sample was heated at 10K per minute up to 350°C. Heating was then continued at 20K per minute up a specified temperature. After the target temperature was attained, the weight was checked several times to confirm that it had attained a constant weight. This marked the end of the ashing process. Subsequently, the weight lost by the sample due to the TG process was measured. A blank test was conducted to determine the amount of ash. The weight of the metal was determined by multiplying the weight loss data by the gravimetric factor for the metal contained as sulfate or oxide. The content of the metal in the sample was calculated according to the following formula:

$$\text{Metal}(\%) = (W-A-B)/f/W$$

For hygroscopic samples, the applicable formula is:

$$\text{Metal}(\%) = (W+C-A-B)/f/W$$

where A: TG weight loss

B: blank test value

C: weight of the cellophane tape

W: amount of sample used

f: gravimetric factor

3. Results and Discussion

3.1 Balance Performance Characteristics

To investigate the sensitivity and the reproducibility of the balance used, a tare weighing approximately 10 mg was fabricated. Using a wind-shielding cover, the mass of the tare was measured repeatedly in a wind-free atmosphere, taking care that the equipment was set at its zero-point for each measurement. The results were a satisfactory sensitivity coefficient = 9.982 mg/10 mg and standard deviation = 0.0021 mg ($n = 11$).

The balance used in this experiment, however, was not equipped with a lock. Therefore, any severe shock occurring when weighing a sample caused a significant shift away from the rest point. Weighing accuracy depends on the technique for operating the balance. To eliminate severe shocks to the balance, a pan stop was put on the magnetic damper. This reduced the magnitude of balance fluctuations created when a sample was either loaded or removed. A tare about the same weight as the sample container was used. These measures ensured

that the balance was always kept at equilibrium, and thus eliminated the hysteresis caused by any large weight fluctuations.

3.2 The Influence of Surrounding Magnetic Field

The electronic balance used in thermogravimetry is susceptible to changes in the surrounding magnetic field. When an object that can change the magnetic field is placed near the balance, the magnet of the balance exhibits different values. As long as the object remains at one place, its effects can be nullified by zero-setting. However, measurement errors may result when the electric furnace is moved after measurement has commenced.

To prevent this effect, parts of the balance were shielded with laminated sheets incorporating amorphous metal flakes (trade name: Amorik Sheet) made by Riken Co⁵⁾. The metallic heat-shielding cylinder for the electric furnace was detached and iron components were removed from the periphery of the balance. The air pump placed at a distance from the equipment. The influence of the magnetic field on the electronic balance was minimized after this manner.

3.3 Heat Insulation for the Balance

The balance used in this work had a temperature coefficient of 0.025 mg/K. The equipment was housed in a thick aluminum block to ensure uniform temperature distribution. To minimize the influence of heat from the electric furnace (for heating the samples) on the balance, cooling water was circulated at the junction between the balance and the electric furnace. A schematic diagram of the junction is shown in fig.1. On the balance enclosed in aluminum block, a cooling base, a height adjusting base, and an electric furnace unit base were stacked in this order. When cold tap water was allowed to flow, the parts of the balance near the electric furnace were cooled, and this disturbed the temperature equilibrium. Combined with the influence of the heat generated by the electric furnace, this produced large baseline fluctuations. When cooling water, maintained at room temperature, was allowed to circulate, the heat generation from the electric balance caused a 0.5K temperature increase in the aluminum block. When the electric furnace was turned on, the heat from the

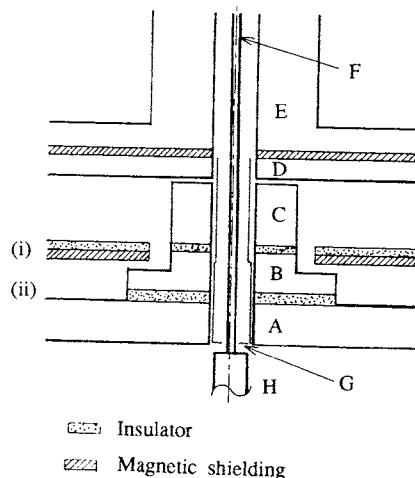


Fig.1 Insulation of TG unit

- A: aluminum block, B: cooling base,
- C: height edjusing base,
- D: furnance installing mount,
- E: electric furnance, F: sample holder unit,
- G: radiation preventive plates, H: balance system.

furnace caused the water temperature to rise after a certain time. The increase in temperature manifested itself as baseline fluctuations in the TG equipment. When cooling water with 10K warmer than room temperature was used, a similar temperature rise in the water was observed. However, the magnitude of this temperature increase was significantly less than when room-temperature water was used.

To stabilize the baseline, the conditions for maintaining the balance at a constant temperature were investigated by inserting a heat insulating material at the junction between the TG electric furnace and the balance (fig.1). The results are shown in fig.2. These results indicate the changes in the baseline that occurred when a sample was heated to 800°C at a rate of 20K per minute and allowed to cool naturally to 80°C. In the figure, a) is the baseline before the modification was made, and b) is the baseline changes that occurred when the encasing unit of the thermal balance, at the position indicated in fig.1 A, was covered with magnetic-shielding and heat insulator materials. When a 10-mm thick spacer was inserted between

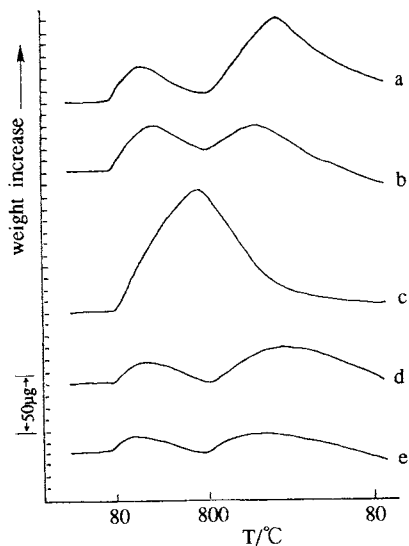


Fig.2 Effects of insulation of TG unit

- a: none terament, b: insulated on TG case(i),
- c: insulated by 10 mm spacer on aluminum block(ii), d: Insulated by 3 mm cork board (ii),
- e: insulated by cork board and cooled with tepid water.

the cooling device (through which the cooling water flowed) and the balance (at the position indicated by fig.1B), the result, was a swelling of the baseline in proportion to the temperature of the furnace as shown in c). This appeared to be due to radiant heat from the electric furnace. Consequently, a 3-mm thick cork board was inserted at the same position to prevent the temperature rise of the cooling device from propagating to the aluminum block. This stabilized the baseline as shown in d). Furthermore, cooling water 10K warmer than room temperature was used. A PVC cooling bag was attached to the bottom of the aluminum block, and the cooling water was allowed to circulate through the bag. This produced favorable baseline for TG measurements, as shown in e). The modified equipment produced few disturbances even when the electric furnace was turned on. The modification also eliminated the need to warm up the balance prior to taking measurements. These innovations made it possible to perform gravimetric measurements with a maximum TG drift of 20 µg

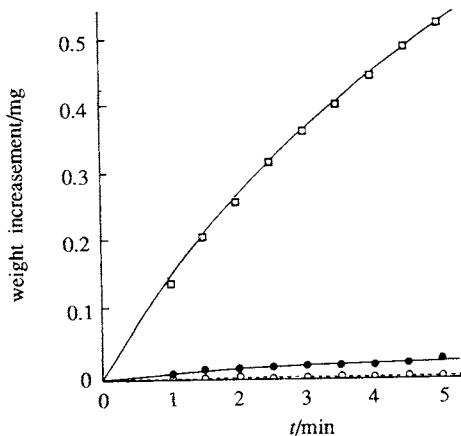


Fig.3 Weight increase of hygroscopic substance
 □: open container, ●: sealed with cellophane tape, ○: wrapped in cellophane tape.

and with a variability of 10 µg or less, where the sample was heated from room temperature to 800°C.

3.4 Techniques for Weighing a Sample

Samples that either release or absorb moisture at room temperature are difficult to weigh accurately. The investigation of methods for preventing weight changes in hygroscopic samples led to the discovery that an accurate and easy-to-use technique was to wrap the sample using adhesive cellophane tape. The weight increase of hygroscopic substance was shown as closed circle in Fig.3. However, one drawback of this technique is that the cellophane tape burns rapidly, and the rapid combustion causes the sample to splash.

This difficulty was overcome by placing a sample at the bottom of the sample container, covering it with a piece of cellophane tape, with the adhesive side facing down, and sealing the sample by affixing the tape to the interior wall of the sample container. Fig.3, the open circle showed time-dependent changes in sample weight observed when this technique was used. When a hygroscopic sample of about 10 mg was weighed, the sample gained approximately 12 µg of water in two minutes. Thus, the technique is effective for preventing an increase of weight during sample measurement to such an extent that it can be ignored.

Table 2 Reproducibility of analysis

| Sample | Calcd. (%) | Found (%) | | | |
|---|------------|-----------|-------|---------|------|
| | | n | mean | deviate | s.d. |
| NaC ₂ H ₃ O ₂ · 3H ₂ O ^{a)} | 16.89 | 5 | 16.95 | +0.06 | 0.07 |
| KC ₂ H ₃ O ₂ ^{b)} | 39.84 | 5 | 39.83 | -0.01 | 0.16 |
| BaC ₆ Cl ₂ O ₄ · 3H ₂ O ^{c)} | 34.48 | 5 | 34.42 | -0.06 | 0.17 |
| Al(C ₅ H ₇ O ₂) ₃ ^{d)} | 8.32 | 5 | 8.28 | -0.04 | 0.17 |
| C ₄₈ H ₄₀ O ₄ Si ₄ ^{e)} | 14.16 | 5 | 14.04 | -0.12 | 0.10 |

- a) Sodium acetate 3-hydrate
- b) Potassium acetate, dried at 150°C, hygroscopic.
- c) Barium chloranilate 3-hydrate, dried at 105°C, hygroscopic.
- d) Aluminum acetylacetonate, ash (Al₂O₃) showed hygroscopic.
- e) Octaphenylcyclotetrasiloxane, ash (SiO₂) showed hygroscopic.

Table 3 Analytical results

| Metal | Sample | Factor | Calcd.(%) found (%) | | |
|-------|--|--------|---------------------|-----------|-----------|
| | | | Calcd.(%) | found (%) | found (%) |
| Na | Na ₃ C ₄ H ₄ O ₆ · 2H ₂ O ^{a)} | 0.3237 | 19.98 | 20.05 | 19.93 |
| | NaC ₇ H ₅ O ₂ ^{b)} | | 15.96 | 16.04 | 16.07 |
| K | KC ₈ H ₅ O ₄ ^{c)} | 0.4488 | 19.15 | 19.01 | 18.92 |
| | K ₂ C ₂ O ₄ · H ₂ O ^{d)} | | 42.45 | 42.39 | 42.46 |
| Mg | Mg(C ₅ H ₇ O ₂) ₂ · 2H ₂ O ^{e)} | 0.2020 | 9.40 | 9.37 | 9.57 |
| | Mg(C ₃ H ₅ O ₃) ₂ · 3H ₂ O ^{f)} | | 9.48 | 9.43 | 9.38 |
| Ca | Ca(C ₂ H ₃ O ₂) ₂ · H ₂ O ^{g)} | 0.2944 | 22.75 | 22.64 | 22.71 |
| | Ca(C ₇ H ₅ O ₂) ₂ · 3H ₂ O ^{h)} | | 14.87 | 14.85 | 15.03 |
| Ba | Ba(C ₂ H ₃ O ₂) ₂ ⁱ⁾ | 0.5884 | 53.77 | 53.84 | 53.64 |
| | Ba(C ₁₀ H ₁₇ O ₂) ₂ ^{j)} | | 28.86 | 28.78 | 28.64 |
| Fe | Fe(C ₅ H ₇ O ₂) ₃ ^{k)} | 0.6994 | 15.81 | 15.80 | 15.84 |
| | Fe(C ₁₀ H ₉ O ₂) ₃ ^{l)} | | 10.35* | 10.34 | 10.52 |

- a: Sodium tartarate, b: Sodium benzoate,
- c: Potassium hydrogenphthalate, d: Potassium oxalate,
- e: Magnesium acetylacetonate, f: Magnesium lactate,
- g: Calcium acetate, h: Calcium benzoate, i: Barium acetate,
- j: Barium cyclohexanebutylate,
- k: Iron(III) acetylacetonate,
- l: Iron(III) tris(phenylbutan dionate)

*: Supplier-certified

4. Analytical Results

Samples were measured repeatedly to study the reproducibility of the technique described above. The results are shown in table 2. Sodium acetate, which contains water of crystallization, is stable at room temperature. Potassium acetate is a highly hygroscopic substance. Accurate results were obtained for these substances when the cellophane tape sealing method was employed. Barium chloranilate, which is hygroscopic and contains chlorine, could be converted into a sulfate by heating it in the presence of sulfuric acid. Aluminum acetylacetonate, which boils at 315°C, is a volatile substance. When heated by the conventional ashing method, in which nitric acid was added to the sample⁶⁾, the sample vaporized and produced a negative value. Treating the sample having a high vapor pressure, it was necessary to add sulfuric acid to decompose the sample into an inorganometallic compound prior to the heating process. The sample of octaphenylcyclotetrasiloxane was treated by adding a drop of dimethylsulfoxide to dissolve it because it is insoluble in sulfuric acid. After dissolving the sample, sulfuric acid was added, and the sample was decomposed by heating. This procedure made the satisfactory results. This technique permitted a quantitative determination of the metal constituents present in the samples with a maximum error of ±0.3% (2σ).

Table 3 shows the results of a quantitative analysis of alkaline and alkaline-earth metals. Samples that tended to foam after decomposition were used in small amounts and were heated gradually. When the sulfate of an alkaline-earth metal was heated to a high temperature, it decomposed and formed an oxide. The result was a weight loss. Alkaline metals were also observed to vaporize at high temperatures, samples containing alkaline metals exhibited a gradual weight loss after the TG curve indicated that they had completed the ashing of samples. Therefore, the ash of a sample must be weighed immediately after the ashing process is completed. In cases where the sulfate of a metal was unstable, accurate results were obtained when the ash of the metal, was weighed as an oxide

Table 4 Analytical results of Aluminum compounds

| Sample | Aluminum | Al content | Titrated(%) | | TG method(%) | |
|--------------------------|----------|------------|-------------|-------|--------------|-------|
| Aspirin | Aluminum | 6.41* | 6.32 | 6.29 | 6.50 | 6.38 |
| Sucralfate | | | 17.70 | 17.71 | 17.73 | 17.81 |
| Al. 3-acetylglucyrrerate | | 1.73 | 1.65 | 1.64 | 1.61 | 1.85 |
| Al. cyclohexane butylate | | 6.66 | 6.57 | 6.57 | 6.63 | 6.54 |
| Al. 2-ethylhexanoate | | 8.17 | 8.17 | 8.16 | 8.18 | 8.23 |
| Al. formacetonate | | | 15.47 | 15.48 | 15.42 | 15.55 |
| Al. chloride 6Aq | | 10.99 | 10.95 | 10.98 | 11.11 | 11.13 |
| Al. nitrate 9Aq | | 7.13 | 7.21 | 7.07 | 7.24 | 7.14 |
| Al. sulfate 14~18Aq | | 8.46* | 8.42 | 8.44 | 8.36 | 8.42 |

*: Supplier-certified

after thermal decomposition of the metal-containing sample. Samples containing iron are shown as examples.

When applied to the analysis of aluminum and silicon, the analytical method described in this paper produces aluminum oxide and silicon dioxide that are highly hygroscopic. These oxides are too hygroscopic to permit accurate gravimetric analysis using the conventional assay procedure involving the use of a micro-muffle tube or a crucible. By contrast, using the method described in this paper, it was possible to obtain accurate gravimetric results, unaffected by the influence of water, even when the sample was heated. Table 4 shows examples of measurements performed on aluminum compounds. Confirming the measured values, values obtained by the wet analysis method⁷⁾ are also given in the table. These values, which are within the $\pm 0.3\%$ tolerance limit for organic micro-analysis, demonstrate the effectiveness of the TG-based ashing method for making a quantitative analysis of organometallic and metal-containing compounds. Many silicon-containing compounds, however, are too unstable, due to hygroscopic decomposition, and these samples are too volatile and flame retardant to permit accurate measurements using this technique.

5. Conclusions

Thermogravimetry was used to investigate possible methods for performing a quantitative analysis of organometallic compounds and metallic salts derived from organic compounds. To improve the accuracy of TG gravimetric analysis, a magnetic

shield was put on the TG equipment. An insulator was inserted to prevent the propagation of heat from the electric furnace to the balance. The water-based cooling system for the balance was reinforced to ensure accurate temperature control. These measurements reduced baseline fluctuations to less than 20 μg during the heating operation when the temperature was allowed to increase from room temperature to 800°C.

Significant improvements were achieved in weighing volatile or hygroscopic samples using the cellophane tape sealing technique. This technique resulted in a measurement accuracy of less than $\pm 0.3\%$ (2σ) when approximately 10 mg of samples were used. Usually, the heating process took approximately one hour, while the conventional method often results in overheating of the decomposition products, causing the ash to splash and decompose and producing negative determination results, the present technique allows the use of a TG curve for observing weight changes in the sample. This prevents any overheating of the sample and ensures accurate measurement of the sample weight upon completion of the ashing process.

Target metals tested for measurement purposes in this work included alkaline and alkaline-earth metals, aluminum, and iron. All yielded satisfactory results. Many organo-silicon compounds, however, failed to yield accurate analytical values due to their high vapor pressures. Some aluminum compounds have shown mixture of aluminum and organic component and ill-defined stoichiometric compositions, this requires methods that are known to produce reliable results for checking the samples. The method presented herein is easy to use and is sufficiently accurate for controlling the process of making aluminum compounds. It is also applicable to samples containing other metals.

6. References

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要 旨

TGを用いた硫酸塩灰化法の検討を行った。TGの正確さを上昇するために次の改良を行った。皿止めを設け試

料容器に等しい重さの代理分銅を用いて常に釣り合わせ、はかりの履歴現象を少くした。断熱剤を炉とはかりとの間に挿入した。温水を流してはかりのケースを一定温度にした。また磁気をシールドした。その結果、800℃までの加熱に対しベースラインの変動を20 μ g以下にすることができた。分析に際して、吸湿性試料はセロファンテープを容器内壁に密着してシールし重量測定を行った。試料をTGに取り付けてゼロにセットした後一滴の硫酸を添加して加熱灰化し残留物の重量を測定した。本法は酸化アルミニウム、酸化ケイ素のように灰分が吸湿性を持つもの、試料が吸湿性や昇華性を示すものの分析にも高い正確さを持って応用できる。分析値は1時間で得ることができ、偏りはなく0.3%以下の誤差(2 σ)で測定することができた。