レポート

Kôtaro Honda-his Thermobalance and his Achievements

Cyril J. Keattch

Introduction

In a comprehensive study of the history and development of thermogravimetry[1], the influence of the Japanese School on the development of the technique is described in detail and from this, it is apparent that the inspiration for the evolution of thermogravimetry came solely from one man, Professor Kôtaro Honda.

He can rightly be credited with producing the first apparatus that constantly recorded mass changes which occurred whilst the sample was subjected to a programmed temperature rise. The paper describing the apparatus and the results obtained was published in 1915[2] and it is, therefore, appropriate that this account of Professor Honda's work should be published in 1990, in recognition of the 75th anniversary of his outstanding invention.

In the opening remarks of this classic paper Honda comments on the difficulties associated with the "ordinary method" of following a chemical change taking place in a compound at high temperatures, ie heating the compound to various temperatures, cooling to ambient temperature and weighing, he continues: "..... it is highly desirable to measure, if possible, the change of weight at high temperatures without cooling to the room temperature. For this purpose, the author has constructed a thermobalance, which admits us to follow continuously the change in its weight at gradually varying temperatures"[3].

A significant point about these opening comments is the manner in which Honda uses the term THERMOBALANCE (..... "the author has constructed a thermobalance") which implies that the term has been in existence for some time. Indeed, the title of the paper is, quite simply, "On a Thermobalance" and yet this is not only the first occasion that such an apparatus is described but also the first occasion that the term "thermobalance" appears in print. In fact, it has yet to be superseded and is now the internationally accepted term[4].

In addition, it is, perhaps, remarkable that such an apparatus should be devised from no apparent earlier foundation; there are certainly no explicit statements in Honda's paper suggesting development from earlier studies. However, a clue emerges when Honda compares the route of thermal decomposition of chromic anhydride with the results obtained, in an earlier paper, by measuring the magnetic susceptibility at different temperatures[5]. Reference to this paper gives no indication as to the origin of the thermobalance, but indicated prior involvement in research into magnetic susceptibility measurements. Indeed, an even earlier paper describes in detail an apparatus for magnetic susceptibility measurements[6], the design of which (Fig 1) shows quite clearly the origins on which Honda based his thermobalance (Fig 2).

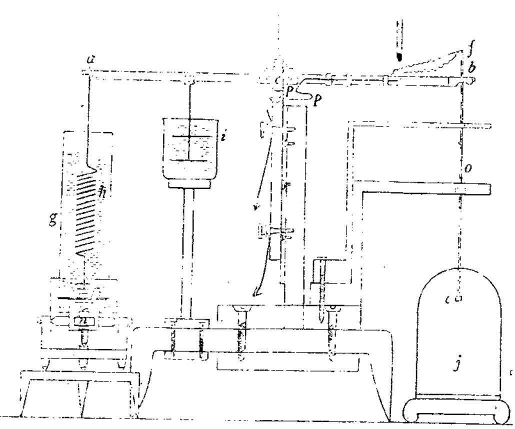

Fig 1 Magnetic Susceptibility Apparatus, according to Honda and Takagi[6].

Industrial and Laboratory Services, PO Box 9, Lyme Regis, Dorset, UK, DT7 3BT

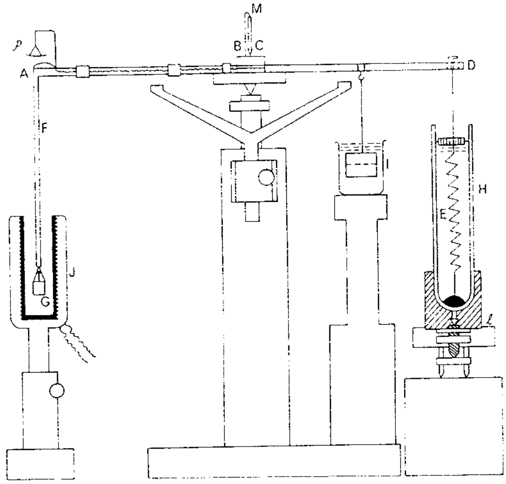

Fig 2 The Honda Themobalance[2].

It is not proposed, in this account, to describe Honda's thermobalance in detail, since this is comprehensively covered in his original publication[2]. However, some points of detail are worthy of note, since they indicate Honda's keen appreciation of the effect of procedural variables on a thermogravimetric experiment. These are currently regarded as standard practice but were only studied in detail some *50 years* after Honda's work[7),8)]:

1. Honda suspended the thermocouple into the sample container, clearly appreciating the importance of the recorded temperature being as close as possible to the sample temperature.
2. The platinum-wire furnace was wound non-inductively. This technique, quite new at the time of Honda's work, produces a furnace having a longer life than a straight-wound furnace and also obviates any anomalous results when dealing with paramagnetic compounds.
3. The temperature increase of the furnace was achieved manually and Honda clearly appreciated the importance of slow heating rates since, typically, the time taken to reach 1000°C was 10–14 hours.
4. Credit must be given to Honda's keen observation in noticing slight weight variations due to the effect of convection, currently referred to as the 'buoyancy effect'.

Honda's Results

The results obtained by Honda are considered to be of sufficient historical importance to be reproduced and commented upon in this communication.

Manganous Sulphate, $MnSO_4$, $4H_2O$

Fig 3 shows the TG curve obtained by Honda, which indicates that water of crystallization is evolved in two distinct stages; between 70° and 110°C three molecules of water are lost, whilst the remaining molecule is released between 230° and 260°C. At 820°C anhydrous manganous sulphate decomposes to form Mn_3O_4 at about 850°C. These results agree well with those obtained by Dollimore[9].

Calcium Sulphate, $CaSO_4$, $2H_2O$

The TG curve of the above compound is reproduced in Fig 4, from which it can be seen that dehydration commences at about 130°C and is complete by approximately 260°C. It

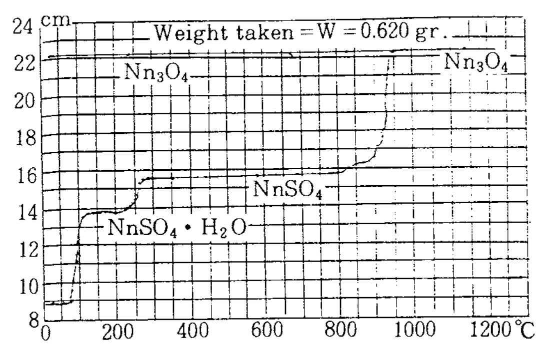

Fig 3 TG Curve of $MnSO_4$, $4H_2O$[2].

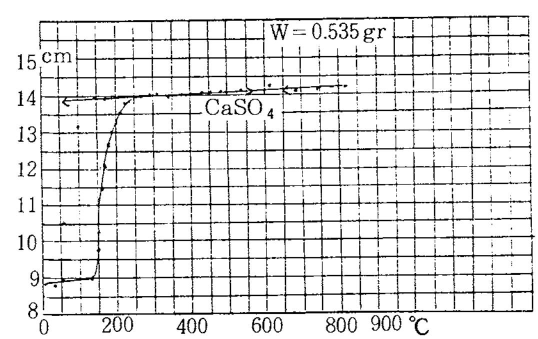

Fig 4 TG Curve of $CaSO_4$, $2H_2O$[2].

will be seen from the details given in Fig 4 that the sample weight was 0.535 g and the total weight loss was 0.116 g. In addition, Honda quotes the mean velocity of separation ie the rate of weight loss, dw/dt as 0.0992 g per hour.

From this information, it has been calculated that; not only did Honda use a heating rate of 4°C per minute but the rate, up to at least 300°C, was remarkably linear, particularly considering that the temperature rise was manually controlled[1]. In addition, by plotting dw/dt, it has been shown that the dehydration of $CaSO_4\ 2H_2O$ is a two stage process corresponding to an initial loss of 1½ molecules of water, followed by a subsequent removal of the remaining ½ molecule of water.

Calcium Carbonate, $CaCO_3$

The thermal decomposition of a 0.455 g sample, obtained by Honda, is given in Fig 5 and shows a single-stage process in which decomposition commences at approximately 500°C and finishes at about 880°C. This is in acceptable agreement with work carried out on a sample of similar weight some 50 years later with considerably more sophisticated equipment[8].

Chromic Anhydride, CrO_3

The rather complicated decomposition pattern, shown in Fig 6, does not agree particularly well with the mode of decomposition proposed by Honda viz: $CrO_3 \rightarrow Cr_6O_{15} \rightarrow Cr_5O_4 \rightarrow Cr_2O_3$.

Nevertheless, Honda claims the results confirm his earlier experiments on the same system using high temperature magnetic susceptibility[5].

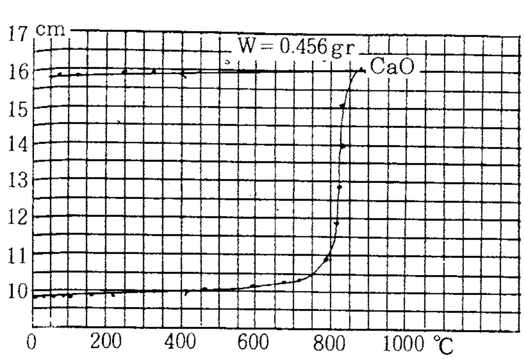

Fig 5 TG Curve of $CaCO_3$.

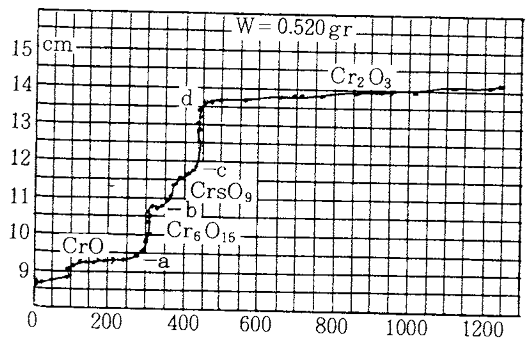

Fig 6 TG Curve of CrO_3.

Honda was a scientist of sufficient experience to appreciate the considerable impact that this paper would have on the scientific community in general and Japanese scientists in particular. However, he pursued the technique of thermogravimetry no further and published no other paper on the subject. He merely concluded his paper with the prophetic words:..... "The investigation also shows the great convenience of using such a balance in similar investigations in chemistry".

The reason for this rather unusual attitude to discovering a new technique can probably be explained by the fact that Kôtaro Honda was primarily a metallurgist and constructed his thermobalance to assist with one small part of his research interests, namely the study of high temperature chemical changes.

Not suprisingly, however, the Honda Thermobalance was produced commercially, by Narusekagaku, Sendai. Production commenced in 1920, several hundred apparatuses were made until production ceased in about 1954[10]. The first production model was acquired by Heikichi Saito, an outstanding scientist and colleague of Honda. He used this thermobalance, together with several of his own modifications and improvements, whilst working at the Kuhara Mining Co. Ltd., where he commenced a basic research programme, resulting in an outstanding thesis, on the chemical changes occurring in metals, oxides and sulphides when subjected to high temperatures[11].

The pioneering work of Honda, followed by the studies of Saito and others, served as foundations on which many rigorous Schools of thermal analysis in Japan were built. They still flourish, 75 years later and will continue to flourish in the future.

Kôtaro Honda, a Brief Biography

No account in celebration of the 75th anniversary of Honda's "Thermobalance Publication" would be complete without a short account of his life.

Kôtaro Honda (Fig 7)[12] was born on 23 February, 1870 in the town of Yahagimachi, in the Aichi prefecture and was the third son of a wealthy farmer, Heizaburo Honda, who spent large sums of money on irrigation work in Yahagimachi. Kôtaro Honda graduated in 1897 from the Department of Physics, Tokyo Imperial University. In the same year as his graduation, he became a lecturer at the Physics Department and was promoted to Professor of Tôhoku Imperial University in 1911. He rapidly achieved fame as an outstanding metallargist and his studies on iron led to his winning, in July, 1916, the Imperial Academy Award. Honda was the main driving force in eastablishing, at the University, in the same year, the Temporary Institute for Physical and Chemical Research, of which he was the first Director. The work of the Institute rapidly achieved national importance and in 1919 it was established as a permanent organization and renamed the Institute of Iron and Steel, with Honda remaining as Director of Research. Under his guidance, the Institute's reputation continued to increase and the activities expanded. This expansion necessitated a further change in title, to The Research Institute for Iron, Steel and other Metals, Tôhoku Imperial University and at this stage Honda became the Institute's first President. After the Second World War a new buidling was constructed (Fig 8)[13] and in honour of his achievements a statue of Honda was erected outside the main entrance.

A Memorial Room is retained at the Institute, containing many of his personal effects. In September, 1975 the Japan Institute of Metals founded a Metals Museum at Aoba Aramaki, Sendai, which also houses several items of interest relating to Honda[14].

Professor Honda received many decorations and awards, the most notable of these being the Cultural Order, in 1937. This Order was conferred personally by Emperor Hirohito and Honda was the first recipient. On 22 November, 1952 the Honda Memorial Foundation was established, in honour of Honda's achievements in the fields of science and engineering. Unfortunately he did not live to see the Foundation develop to any extent, since he died on 12 February, 1954.

Fig. 7 Kôtaro Honda.

Fig 8 The Research Institute for Iron, Steel and other Metals, Tôhoku University.

References

1. C J Keattch, PhD Thesis, University of Salford, UK, 1972.
2. K Honda, *Sci. Rep. Tôhoku Univ.* **4**, 97–103 (1915).
3. Idem ibid
4. R C Mackenzie, C J Keattch, D Dollimore J F Forrester, A A Hodgson and J P Redfern, *Talanta* **19**, 1079–1081 (1972).
5. K Honda and T Sone, *Sci. Rep. Tôhoku Univ.* **3**, 223–230 (1914).
6. K Honda and H Takagi, *Sci. Rep. Tôhoku Univ.* **1**, 229–242 (1911).
7. E L Simons and A E Newkirk, *Talanta* **11**, 549–571 (1964).
8. A E Newkirk and E L Simons, "Comments on the Intepretation of Dynamic Thermogravimetric Curves", General Electric, Report No. 65-c-018, September, 1965.
9. D Dollimore, Private communication.
10. H Saito, Personal interview by the author, 14 November, 1976, accompanied by Profs Yasutoshi Saito and Ryohei Otsuka.
11. H Saito, *Sci. Rep. Tôhoku Univ.* **16**, 37–200 (1927).
12. The author is indebted to Prof Ryohei Otsuka (Waseda University) who kindly supplied some biographical notes and the photograph of Kôtaro Honda.
13. Photograph kindly supplied by Prof Dr Hiroshi Watanabe, sometime Director of the Institute.
14. Further information on Kôtaro Honda, including some interesting photographs may be found in the following books: "The Life of Kôtaro Honda" by Teijiro Ishikawa, 3rd edn, Honda Memorial Foundation, Sendai, 1973. "A Memorial to Kôtaro Honda – contributions from his Students", Seibundoshinkosha, Tokyo, 1955. Copies of these books were kindly presented to the author by Prof Dr Hiroshi Watanabe, sometime President of the Board of Trustees, Honda Memorial Foundation on behalf of the Foundation.

Curriculum Vitae

Cyril Keattch first took an interest in thermal analysis some 30 years ago, when engaged on precious metal research with the Platinum Metals Division, International Nickel Co. (Mond) Ltd.

He was subsequently appointed Chief Analyst with the civil engineering firm of John laing Research and Development Ltd. and soon realised the considerable potential that thermogravimetry had in the field of building materials. Several thermogravimetric procedures used in this sphere were due to his endeavours.

In 1966 he left the laboratories of John Laing Research and Development Ltd. to start up as an independent consultant and included thermal methods in his sphere of activities. He subsequently became interested in the histroical aspects of thermogravimetry and in 1977 obtained the degree of Doctor of Philosophy form the University of Salford with a thesis entitled "The History and Development of Thermogravimetry", which is now regarded as the authoritative work on the subject.

He has lectured extensively on thermogravimetry, is Honorary Secretary and a founder member (1965) of the Theraml Methods Group of the Analytical Division, Royal Society of Chemistry and also the first (and only) Honorary Secretary of the Nomenclature Committee of the International Confederation for Thermal Analysis (ICTA). He is, in addition, Editor of ICTA News and more recently was appointed Secretary of the Organizing and Scientific Committees of the 10th ICTA Congress.

著者の紹介と執筆の経緯

本文中の文献 1)に示されているように，著者Dr.Cyril J. Keattchは本多光太郎博士の業績の科学史的研究により博士号を授与されている。これは，文献10， 12～14）からも明らかなように，著者自身が来日し，実際に調査した結果をふまえて達成されたものである。著者の第一の関心事は，本多博士の有名なKS鋼の発明ではなく，熱天秤の発明と熱重量測定の創始であった。

本年は熱天秤と熱重量測定に関する本多博士の初めての論文が出版されてから満75年にあたる。この日本が誇るべき熱分析における業績を，日本熱測定学会が看過することはできない。これは日本の傑出した基礎研究の成果であり，欧米で熱重量測定が初めて行われたのは，10年後，フランスDuvalによってであった。この年には，日本において熱重量測定結果の速度論的解析が，理化学研究所の鯨井，赤平両氏により発表されている。この事実を見ても，本多博士の優れた業績と日本の高い水準とが明らかであろう。この観点から，執筆が依頼され，この点を十分認識されている著者は快く書いてくださった。

Dr. Cyril J. Keattchは，約30年前，International Nickel Co（Mond）Ltdの白金属金属部で貴金属の研究に従事している時に，初めて熱分析に関心をもった。彼は，その後，John Laing研究開発会社の土木技術部門のChief Analystに任命され，建築材料分野における熱重量測定の大きな可能性をすぐに認識した。

1966年，上記研究開発会社を去り，自営のコンサルタント業を始め，その分野に熱分析技法を取り入れた。その後，熱重量測定の歴史的側面に興味を持つようになり，1977年，The History and Development of Thermogravimetryと題する学位論文をSalford大学に提出して，Doctor of Philosophyの学位を得た。

彼は熱重量測定につき広範な講義を行ってきており，イギリス化学会分析化学部会熱測定グループの創立メンバーであり（1965），名誉幹事である。また，国際熱分析連合（ICTA）用語法委員会の初めの，そして唯一の，名誉幹事である。さらに，ICTA Newsの編集者を努め，最近，第10回国際熱分析会議の組織委員会及び科学委員会の幹事に指名された。

なお，著者は日本人にも分りやすい英語を話されることで知られており，本文も平明な英語で書かれているので，原文のまま，掲載することになった。

（文責　小沢丈夫）