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THERMAL INVESTIGATIONS ON γ-RADIATION PROCESSED NATURAL MEDICINAL PRODUCTS (ASHWAGANDHA, AMLA AND HARTIKI)

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Abstract

DSC and TG studies were carried out on γ-radiation processed Indian natural products of medicinal importance, namely Ashwagandha (Withania Somnifera), Amla (Emblica Officinalis) and Hartiki (Terminalia chebula). DSC thermoanalytical curves were recorded from 35 to 400°C in air and nitrogen atmosphere. Similarly, TG thermoanalytical curves were taken from 35 to 700°C in air and nitrogen atmosphere. Irradiated products gave significantly different thermoanalytical profiles in comparison to non-irradiated samples. The differences were observed above decomposition temperature of 200°C and were non-linear with respect to radiation dose. Partial oxidation of the products during irradiation in air could be responsible for the observed differences.

Keywords: Co-60 γ-radiation, DSC, herbal medicine, TG

Introduction

Herbal products are widely used in recent years as holistic medicine to treat several diseases [1]. Three Indian products namely Ashwagandha, Amla and Hartiki are used under Ayurvedic medicine. These products are known to possess several beneficial properties [2–5] and are used for treating diseases. Amla is known for rich source of vitamin C. Herbal/plant products are natural in origin and often contain high microbial contaminations and therefore, are treated with one of the methods including heat, ethylene oxide and radiation in order to reduce the microbial contamination [6]. Irradiation, using Cobalt-60 γ-radiation and electron beam radiations is commonly employed for treating these products. The products are generally exposed to radiation doses between 10 to 30 kGy to achieve the desired decontamination level. The products, being raw and from plant origin, contain several ingredients. Besides containing active ingredients, several constituents like cellulose, carbohydrate, lipids, proteins, vitamins, minerals, etc. are also integral part of the ream product. Investigating such complex products with specific techniques may not reveal small changes in the product due to radiation treatment.

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Irradiation as such may degrade some of the constituents of the products and might produce free radicals which are highly reactive. The radicals react with oxygen and form oxidation products like oxides and peroxides. These may exothermally decompose at higher temperatures to give variations in thermal profiles. Presence of moisture in the product during irradiation can also influence thermal profiles. It is due to the radiation chemistry of water, forming hydroxyl, hydrogen radicals and hydrogen peroxide which might react with the ingredients forming new products. These changes are known to be negligible at the treatment dose and difficult to detect in bulk products. Thermal analysis had been used in past, to correlate general chemical composition and decomposition profiles of herbs, different parts of plants and other natural products [7–9]. No literature could be found on thermal analysis of irradiated herbal products. In the present work, thermal studies were carried out on the bulk raw products to ascertain any changes in thermal behavior which might be introduced due to irradiation [10].

Experimental

Ashwagandha, Amla and Hartiki powders were procured from local market and used as received. Mettler DSC and TG instruments (TA-3000) were employed for the thermal studies. About 10 mg of the irradiated and non-irradiated (Control) samples were used for the analysis. The samples were heated in aluminium crucibles at a heating rate of 10°C min^{-1} in air (50 mL min^{-1}) between 3 to 400°C for DSC analysis. Similarly, samples were heated in alumina crucibles between 35 to 700°C at 10°C min^{-1} under air atmosphere in TG analysis. To avoid oxidation and to resolve changes, the samples were also heated in nitrogen atmosphere (50 mL min^{-1}) in DSC and TG analysis. Average of three readings were taken for record. All the data values were normalized to 100 mg sample mass.

Results and discussion

DSC profiles of Ashwagandha in air and nitrogen atmosphere are shown in Figs 1 and 2, respectively. In the DSC profile of non-irradiated product (0 kGy), the exothermic peak of oxidation at 301°C is very sharp (1167 J g^{-1}). With increase of dose, the peaks become broader for 10 kGy (372 J g^{-1}) and 25 kGy (716 J g^{-1}) samples (Fig. 1). This non-linear behavior could be due to partial oxidation of the samples during irradiation and thus reducing extent of oxidation reactions which otherwise occur on heating non-irradiated sample. DSC profile in nitrogen atmosphere (Fig. 2) shows broad peak for non-irradiated sample in comparison to flat peaks of irradiated samples. These peaks are not well defined for integration. In the absence of oxygen, this could be due to exothermic decomposition of the ingredients. There are no significant differences in TG profiles of the irradiated and non-irradiated samples heated in air (Fig. 3). TG profile in nitrogen atmosphere shows decreased mass loss in 125 to 325°C step and increased mass loss between 325 to 450°C step for irradiated samples (Fig. 4 and Table 1).

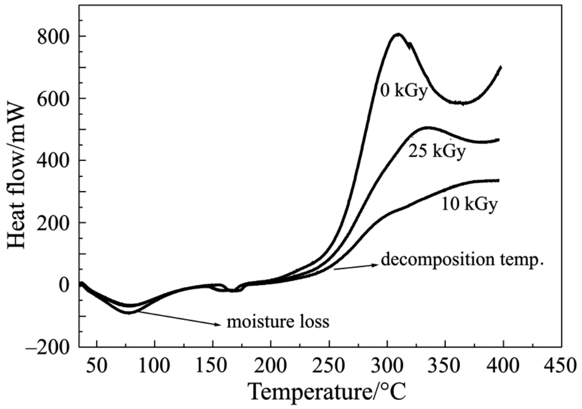

Fig. 1 DSC profiles of γ-irradiated Aswagandha in air

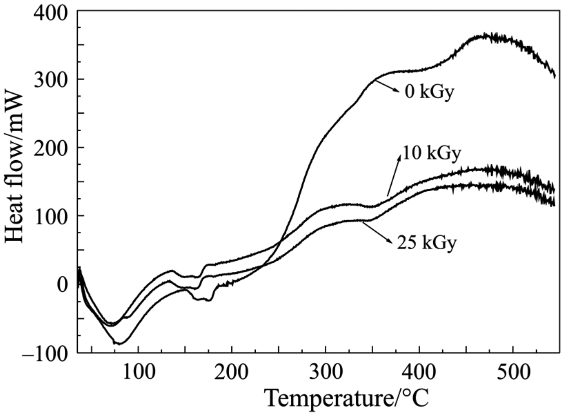

Fig. 2 DSC profiles of γ-irradiated Aswagandha in nitrogen

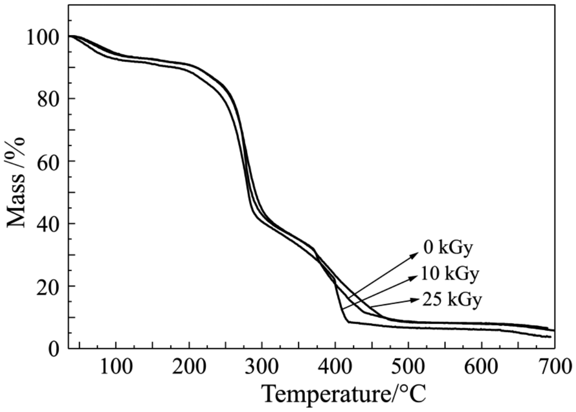

Fig. 3 TG profiles of γ-irradiated Aswagandha in air

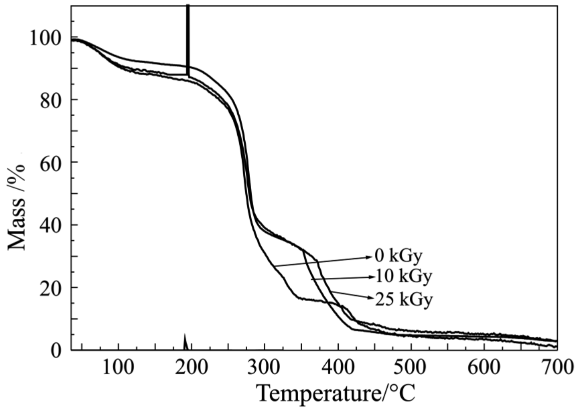

Fig. 4 TG profiles of γ-irradiated Aswagandha in nitrogen

Table 1 Mass loss (%) of γ-irradiated Aswagandha in air and nitrogen atmosphere

Temperature/°C	Mass loss of γ-irradiated Aswagandha in air and (nitrogen)*		
	0 kGy	10 kGy	25 kGy
35–125	6.88 (9.41)	8.18 (10.74)	6.87 (11.12)
125–325	55.07 (70.32)	55.07 (53.51)	54.70 (52.77)
325–450	27.21 (12.46)	29.08 (28.93)	25.90 (29.35)

*Values in brackets are for samples heated in nitrogen atmosphere

DSC profile of Amla in air shows an endothermic peak at 190°C (Fig. 5). The peak areas get reduced in irradiated samples (non-irradiated=37 J g^{-1}, 10 kGy=18 J g^{-1} and 25 kGy=22 J g^{-1}). Another exothermic peak is observed at 339°C. Samples heated in nitrogen gave similar DSC profiles (Fig. 6). The enthalpy values at 190°C were 9,

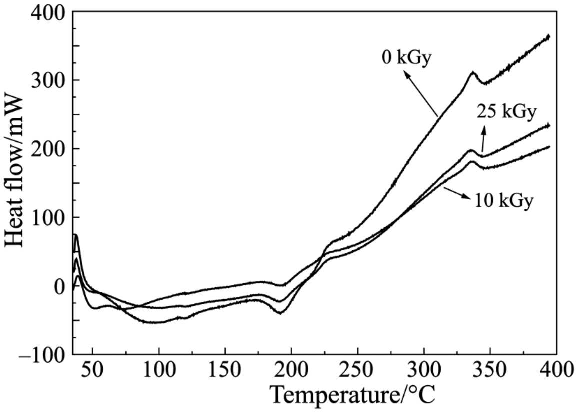

Fig. 5 DSC profiles of γ-irradiated Amla in air

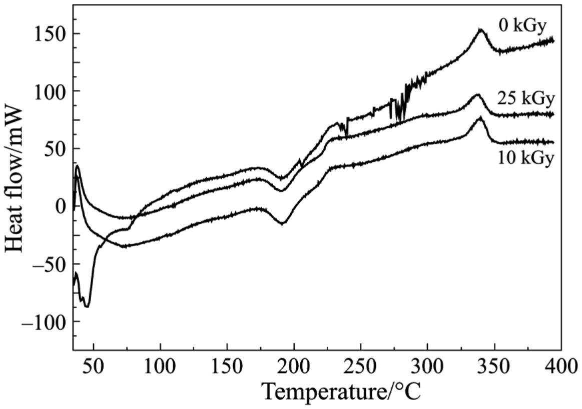

Fig. 6 DSC profiles of γ-irradiated Amla in nitrogen

11.5 and 11 J g^{-1} for control, 10 and 25 kGy samples, respectively. These values are significantly lower than the samples heated in air. Non-irradiated sample shows higher exothermicity in comparison to irradiated samples (10 and 25 kGy). DSC profiles clearly distinguish between irradiated and non-irradiated samples.

TG profile of Amla in air and nitrogen are shown in Figs 7 and 8, respectively. TG in air gave five decomposition steps which changes to three steps in nitrogen atmosphere. Samples heated in nitrogen gave significant different mass losses in comparison to samples heated in air. No significant differences were observed in the decomposition profiles and mass losses of non-irradiated and irradiated samples heated in air. Samples heated in nitrogen atmosphere showed decreased mass losses between 250 to 500°C (Table 2).

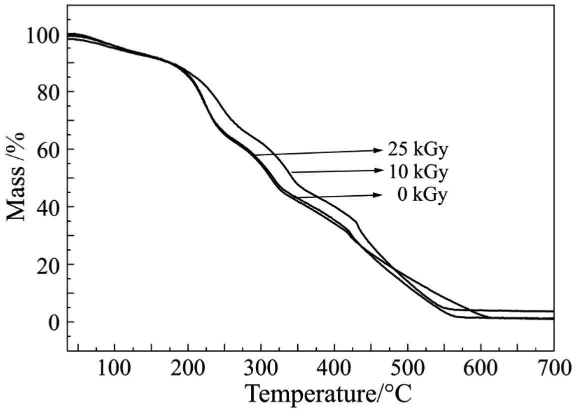

Fig. 7 TG profiles of γ-irradiated Amla in air

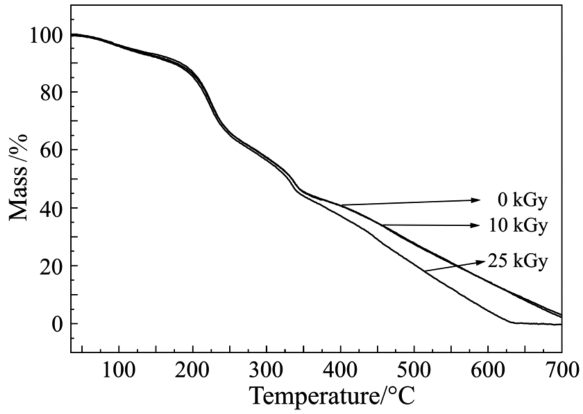

Fig. 8 TG profiles of γ-irradiated Amla in nitrogen

Table 2 Mass loss (%) of γ-irradiated Amla in air and nitrogen atmosphere

Temperature/°C	Mass loss of γ-irradiated Amla in air and (nitrogen)*		
	0 kGy	10 kGy	25 kGy
35–125	6.69 (5.65)	6.59 (5.71)	6.71 (6.44)
150–250	27.11 (27.02)	19.08 (27.82)	27.23 (26.99)
250–500	49.40 (38.19)	58.92 (37.39)	52.56 (44.55)

*Values in brackets are for samples heated in nitrogen atmosphere

Hartiki sample irradiated to 25 kGy showed significantly different DSC profile above decomposition temperature of 250°C in relation to non-irradiated and 10 kGy irradiated samples (Figs 9 and 10). TG profiles (Figs 11 and 12 and Table 3) showed

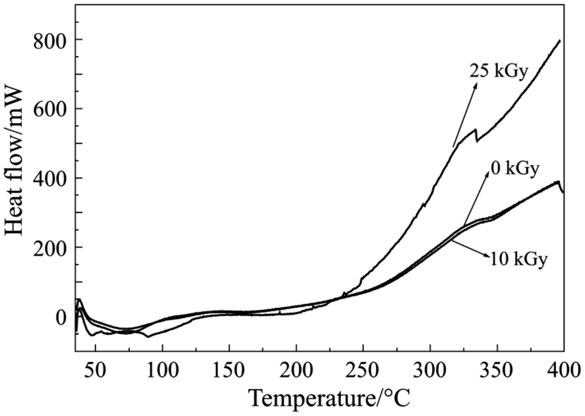

Fig. 9 DSC profiles of γ-irradiated Hartiki in air

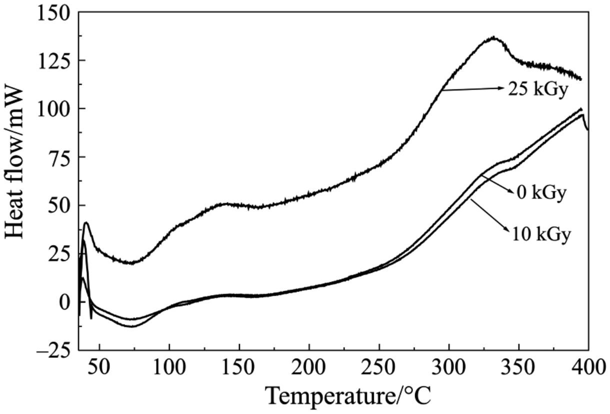

Fig. 10 DSC profiles of γ-irradiated Hartiki in nitrogen

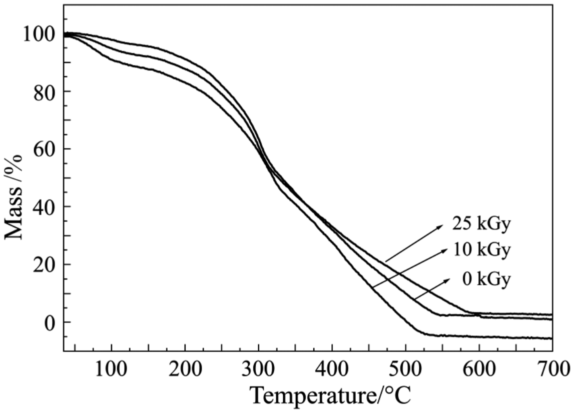

Fig. 11 TG profiles of γ-irradiated Hartiki in air

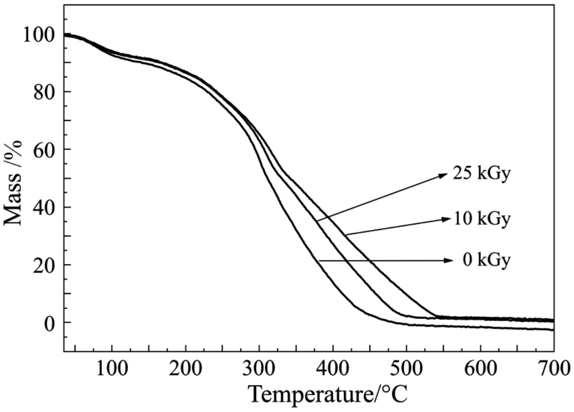

Fig. 12 TG profiles of γ-irradiated Hartiki in nitrogen

Table 3 Mass loss (%) of γ-irradiated Hartiki in air and nitrogen atmosphere

Temperature/°C	Mass loss of γ-irradiated Hartiki in air and (nitrogen)*		
	0 kGy	10 kGy	25 kGy
35–125	3.63 (9.29)	11.02 (7.71)	7.04 (8.09)
200–400	59.09 (70.93)	55.30 (52.16)	54.61 (59.34)

*Values in brackets are for samples heated in nitrogen atmosphere

non-linear differences in mass losses between non-irradiated and irradiated samples. Irradiated samples heated in nitrogen atmosphere showed lower mass losses between 200–400°C (Table 3). No specific correlation was observed between dose and thermal effects.

The results of present study do indicate that some changes occur in the products on irradiation. The observed differences in the results could not be attributed to specific reactions as the products contain several ingredients. On macroscopic scale, one could relate these observations to partial oxidation and other changes that might occur during irradiation. Formation of oxidation products and breaking of bonds between active ingredients and supporting matrix like cellulose, protein, etc. during irradiation and heating can give varying enthalpy values and mass changes on heating non-irradiated and irradiated samples. This observation is also supported by reported increase in antioxidant property of irradiated Amla powder due to improved extractability of active ingredients [11]. Since the powders are a complex blend of several constituents, irradiating and then heating such products (P–P) could be represented as

$$\text{P–P}\rightarrow\text{P.+P. (thermal decomposition, free radicals)} \qquad \text{I}$$

$$\text{P–P}\rightarrow\text{P.+P. (radiation formation of free radicals)} \qquad \text{II}$$

$$\text{P.+O}_2\rightarrow\text{PO}_2\text{. (peroxide)} \qquad \text{III}$$

$$\text{PO}_2\text{.+P–P}\rightarrow\text{PO}_2\text{H+P–P. (hydroperoxide formation, chain reaction)} \qquad \text{IV}$$

$$\text{P–P.+O}_2\rightarrow\text{P–PO}_2 \qquad \text{V}$$

$$2\text{PO}_2\cdot\text{–}\rightarrow\text{POO–OOP} \qquad \text{VI}$$

Reaction I could occur even on heating and is endothermic in nature. Reaction II to reaction VI could occur during irradiation and on thermal decomposition at higher temperatures in the presence of air. Some of the oxidized products shown in reactions III to VI are formed during irradiation itself. Heating the samples in nitrogen atmosphere would reduce the extent of reactions III to VI. Reactions IV and V could ensue exothermic chain reactions. Peroxides and hydroperoxides formed during irradiation could affect the decomposition profile as observed in DSC and TG in a non-linear way. The formation and decomposition of these oxides are generally exothermic. When formed during irradiation itself, these reactions do not take place during thermal decomposition and thus lower exothermicity as seen in irradiated Amla above 200°C. There is higher concentration of free radicals at increased radiation doses [6]. Therefore, relatively more of these reactive free radicals could be present during thermal decomposition in air contributing larger enthalpy values. Non-linear behaviour in decomposition profiles could be attributed to sum of these reactions as seen in Aswagandha (Fig. 1). The extent of these reactions would vary due to environmental conditions during irradiation, irradiation dose and amount of formation and decomposition of these products during irradiation and heating. These changes are small at treatment doses. Decomposition of the samples at higher temperature as observed in DSC and TG in the present study does indicate oxidative changes occurring during irradiation with respect to non-irradiated samples.

Conclusions

Thermal investigations on Ashwagandha, Amla and Hartiki show that there is partial oxidation of the product during irradiation. The changes occurring during irradiation are reflected in decomposition profiles of the products on heating. These changes have been observed to be non-linear with respect to radiation dose. Thermoanalytical curves of the products could be useful for identification and distinguishing between non-irradiated and irradiated Aswagandha, Amla and Hartiki samples.

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