NEUTRON ACTIVATION ANALYSIS OF PETROLEUM FEEDS AND PRODUCTS OF A CATALYTIC CRACKING UNIT

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Na, Al, S, Cl, V, Mn, Ni, As, Br, I, La, Eu and Dy were determined in 2 feeds and 5 products of a catalytic cracking unit. Catalysts used in this unit were also analyzed and 18 elements were measured in this matrix. The overall mass balance of the unit was calculated and it was shown that the concentrations of most elements are reduced during cracking but the concentrations of some others (Al, Dy, Eu and La) are increased.

Introduction

Petroleum and its derivatives are the principal energy source in Canada: in 1978 alone, 98 billion litres of hydrocarbons were consumed in this country. It is a well-known fact that petroleum contains small concentrations of trace elements which are released into the environment during combustion, some of which are either toxic or carcinogenic.

Several attempts have been made in the past to explain the origin of trace elements in crude oil, but not very much attention was paid to the source of trace elements in the final products. From a practical standpoint, this is an important question considering the fact that these are the products which are in everyday use in homes and factories. The composition of petroleum products depends on the composition of crude oil and on the chemical interactions which take place in refineries. One procedure which is widely used is catalytic cracking, and the basic purpose of this work is thus the analysis of feeds and products of a catalytic cracking unit and the establishment of the mass balance of trace elements in the refining process.

Instrumental neutron activation is an excellent method for the analysis of petroleum and its derivatives for trace elements. Using this technique, up to 29

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elements can be determined non-destructively and with high sensitivity. As was established previously in this laboratory, the accuracy and precision which can be obtained by this method are very good.

**Experimental**

Petroleum samples were obtained in 1 litre lots from a refinery in the Montreal area. Each bottle was shaken and a 0.5 g sample was transferred into a clean 1.5 cm³ polyethylene vial which had been washed previously with concentrated nitric acid and distilled water. Standards, in the form of aqueous solutions, were prepared from reagent-grade non-hygroscopic chemicals. The samples and standards were placed into 7 cm³ polyethylene vials, heat-sealed, and irradiated for 2, 30 and 240 minutes in the SLOWPOKE Nuclear Reactor. A thermal neutron flux of $10^{12}$ n·cm⁻²·sec⁻¹ was used for all activations. In order to eliminate errors due to impurities in the polyethylene vials, the radioactive samples were transferred into new vials and weighed. Preliminary tests have indicated that small and variable amounts of trace elements were present in these vials. After irradiation, the samples were left to decay for 2 minutes, 1 hour and 60 days. Gamma-ray spectra were collected in the live-time mode for 600, 2000, 10,000 and 80,000 seconds with a Ge(Li) Detector and a Canberra 8180 Analyzer. The dead-time of the analysis system was kept below 20% by choosing appropriate irradiation conditions.

The Ge(Li) Detector has an efficiency of 6.6% relative to a 7.5 × 7.5 cm NaI(Tl) Detector and its resolution is 1.9 keV for the 1333 keV $^{60}$Co line. After counting, the spectra were analyzed and peak areas calculated. From this information, concentrations and detection limits were obtained.

The nuclear reactions observed, the photopeaks used and possible interferences are presented in Table 1. The precision and accuracy of the method and the treatment of interferences were discussed previously.

**Results and discussion**

The trace element compositions of the different feeds and products of a catalytic cracking unit are presented in Table 2. The production characteristics and physical properties of the cracking products studied are listed in Table 3, and a schematic diagram of the circulation of petroleum in the catalytic cracking unit is shown in Fig. 1. The catalytic unit in question contains 225 tons of catalyst and the average residence time of the feed is 6 seconds. The catalyst is lost at a rate of 1.5—2 tons/day. The trace and minor element composition of the catalyst