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ATOMIC ENERGY OF CANADA LIMITED

L'ÉNERGIE ATOMIQUE DU CANADA LIMITÉE

THE ANALYSIS OF HYDROCARBONS BY DUAL-ENERGY GAMMA-RAY DENSITOMETRY

L'analyse d'hydrocarbures par la densitométrie à rayons gamma à double énergie

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Résumé

Plusieurs hydrocarbures ont été analysés par une méthode non-envahissante utilisant la densitométrie à rayons gamma à double énergie. Le rapport atomique hydrogène/carbone a été déduit pour des hydrocarbures purs tandis que pour des échantillons provenant des processus d'huile lourde, la teneur de cendres a été inféreé.

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ABSTRACT

Various hydrocarbons have been analyzed noninvasively by dual-energy gamma-ray densitometry. The hydrogen/carbon atomic ratio was deduced for pure hydrocarbons while for heavy oil process samples, the ash content was inferred.

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1. INTRODUCTION

The depletion of conventional fuel reserves and the increase in the price of crude oil have combined to generate renewed interest in the upgrading of heavy crudes, oil shales, tar sands and coals (1). Direct hydrogenation, the most promising of several upgrading processes presently under development, converts heavy oils to light distillable fractions while reducing sulphur content. Conversion of coals into liquid fuels could be important in the near future (2). In many of these processes, ash concentrations must be monitored (3,4). The traditional chemical analysis of grab samples is time consuming and, perhaps more significantly, perturbative. Rapid non-intrusive nuclear techniques, in particular dual-energy gamma-ray densitometry (DGD), may constitute a viable alternative.

The DGD method is based on the energy dependence of the transmission of a gamma-ray beam incident on a hydrocarbon. At moderate gamma-ray energies, two mechanisms contribute to the removal of photons from the beam. The photoelectric effect, which is proportional to the fourth power of the atomic number, dominates at lower energies, while at higher energies, the Compton effect, which is directly proportional to the atomic number, prevails. Consequently, at lower energies the attenuation cross-section of carbon, for example, is more than 1300 times greater than that of hydrogen, whereas at higher energies they differ by only a factor of six.

The DGD method has been applied elsewhere to the analysis of ash in coal (5-7). The analysis of hydrocarbon liquids is reported here. The determination of hydrogen/carbon atomic ratios for pure hydrocarbons will be described in addition to the measurement of ash content for heavy oil process samples. But first, the underlying theory of DGD will be developed.

2. THEORY

The attenuation of a narrow beam of photons of energy E_i by an absorber of thickness x is governed by (8)

$$I_i/I_{i0} = \exp\left(-\sum_j \sigma_{ij} N_j x\right) \qquad [1]$$

where

I_i is the intensity of the attenuated beam,

I_{i0} is the intensity of the unattenuated beam,

σ_{ij} is the attenuation cross-section per atom of the j^{th} element of the absorber for the energy E_i, and

N_j is the number of atoms of the j^{th} element per unit volume of the absorber.

If the photon attenuation is measured at two energies E_1 and E_2, an attenuation ratio R can be constructed as follows:

$$R = \ln (I_1/I_{10})/\ln(I_2/I_{20}). \qquad [2]$$

Then substituting [1] into [2] yields

$$R = \sum_j \sigma_{1j} N_j \; / \; \sum_j \sigma_{2j} N_j. \qquad [3]$$

It is now apparent that the attenuation ratio is independent of the amount of the absorber, depending only on the composition of the absorber and known attenuation cross-sections.

If the absorber is comprised of two elements only, Eq. 3 can be solved for the atomic ratio:

$$\frac{N_1}{N_2} = \frac{\sigma_{12} - R\sigma_{22}}{R\sigma_{21} - \sigma_{11}}. \qquad [4]$$

In order to optimize the design of an instrument based on the DGD principle, one must develop an appreciation of the factors that influence the uncertainty in the measurement. The uncertainties associated with counting statistics are a primary concern for any nuclear instrument. Fortunately, the propagation of statistical uncertainties through Eqs. [1], [2] and [4] can be calculated relatively straightforwardly. Figure 1, for example, shows the calculated error in the hydrogen/carbon atomic ratio as a function of the energy of the low-energy gamma ray assuming an energy of 100 keV for the high-energy gamma ray. The absorber is a 50 mm thickness of a hydrocarbon with a density of 1.0 $kg.L^{-1}$ and a hydrogen/carbon atomic ratio of 1.5. A minimum uncertainty of approximately two percent is achieved at about 15 keV supposing that 10^6 photons are incident on the absorber. At lower energies the beam is so strongly attenuated that the residual count rate is insignificant; at higher energies the sensitivity to differences in atomic number is reduced. The error is relatively insensitive to the energy of the high-energy gamma ray provided that the energy is significantly higher than that of the low-energy gamma ray.

The optimum energies for DGD are strongly dependent on the characteristics of the absorber. Figure 2 shows the optimum energy of the low-energy gamma ray as a function of absorber thickness. Obviously, the variation with the density of the absorber is analogous. The optimum varies very little with the hydrogen/carbon atomic ratio.

There are, of course, other factors that contribute to the overall measurement uncertainty, such as inhomogeneities in the hydrocarbon, but these are usually beyond the control of the instrument designer.

3. EXPERIMENT

A laboratory demonstration of DGD has been conducted with a 370 MBq (10 mCi) source of ^{109}Cd which emits 88.0 keV gamma rays and X rays with an average energy

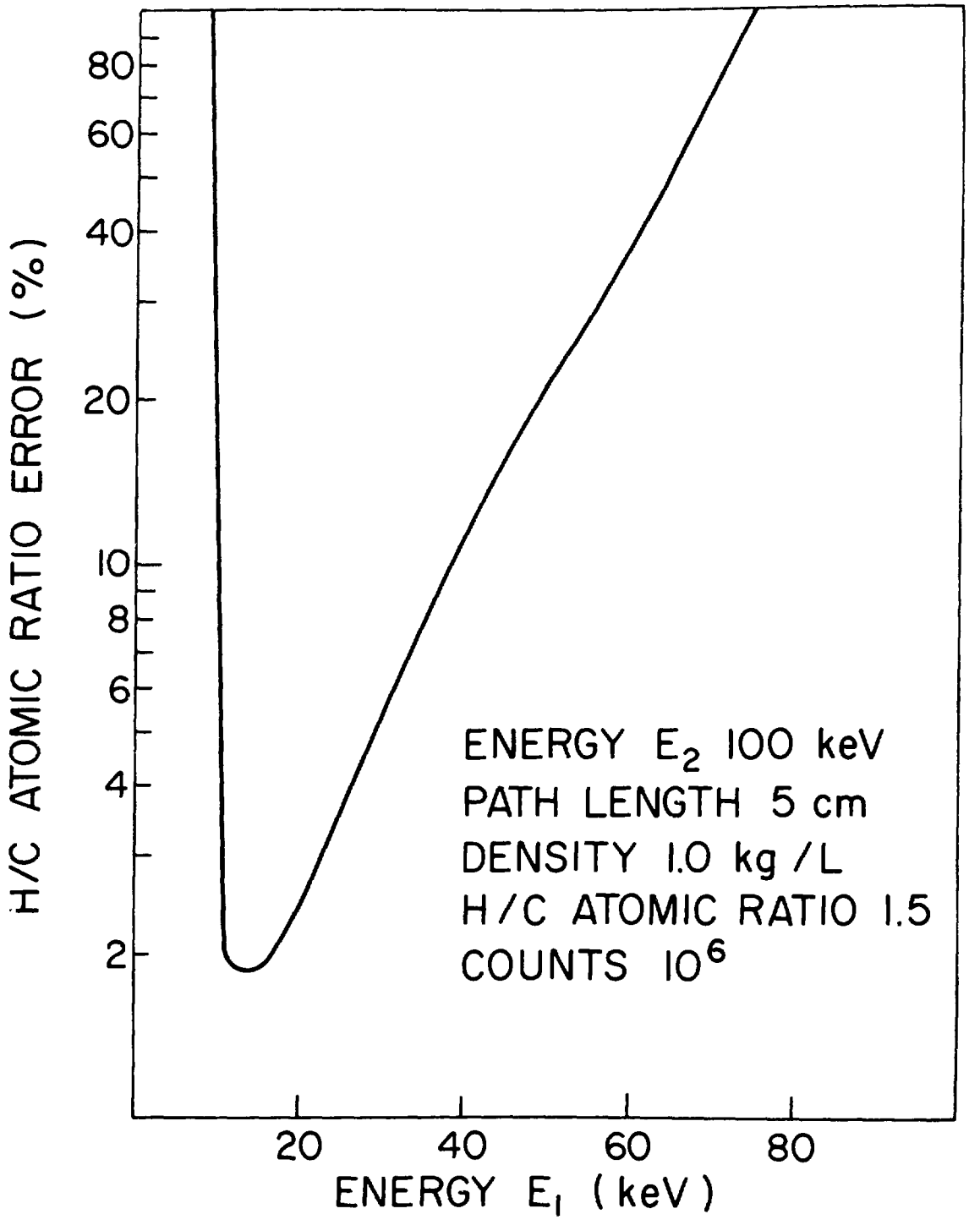

Figure 1: Statistical uncertainty in hydrogen/carbon atomic ratio as a function of the energy of the low-energy gamma ray.

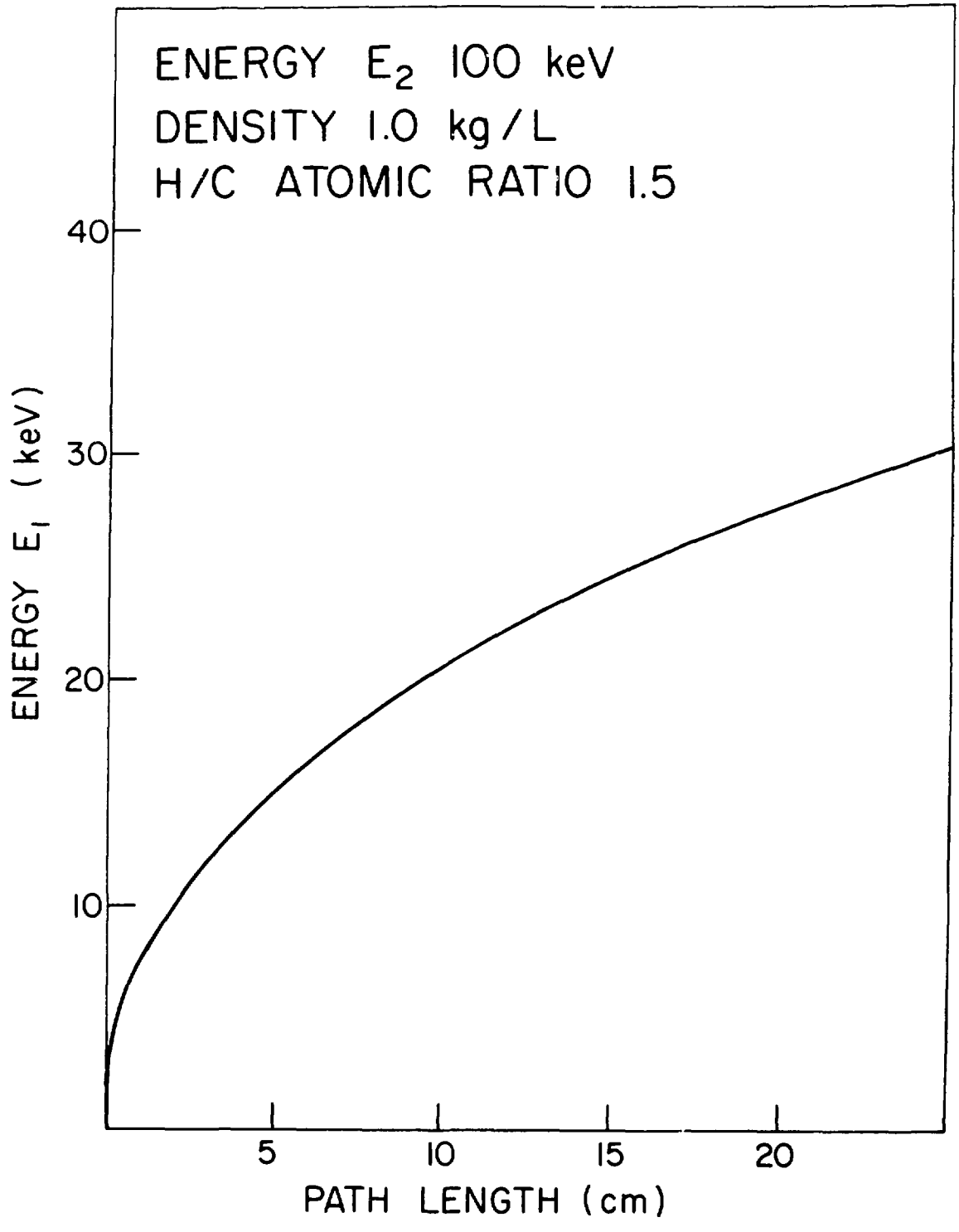

Figure 2: Optimum energy for the low-energy gamma ray as a function of the specimen thickness.

of 22.6 keV. The photons were detected by a NaI(Tℓ) scintillator 19 mm in diameter by 38 mm high mounted on a 19 mm diameter photomultiplier tube. Both the source and the detector were tightly collimated, so that the transmitted beam of X rays and gamma rays subtended only 1.1 degrees. Thus scattered photons were almost totally excluded, virtually eliminating a potential source of sample thickness dependence. The collimators were made of mild steel, thus avoiding the contamination of the photon spectra by fluorescent X rays from the more traditional high atomic number materials (e.g. lead fluoresces at 87.3 keV).

The data acquisition system consisted of a preamplifier, an amplifier, a spectrum stabilizer and a multichannel analyzer.

Liquid hydrocarbons were analyzed in thin walled polyethylene vessels having a volume of 43 mL. Solid hydrocarbons were machined into right circular cylinders 51 mm by 51 mm for analysis.

Several photon spectra were required for each analysis. In addition to the obvious measurement with the specimen in the beam, a normalization spectrum was collected periodically with the specimen chamber empty or filled only by an empty polyethylene vessel, depending on whether the specimen was solid or liquid. Occasionally, a lead cylinder was substituted for the specimen, generating a background spectrum.

4. RESULTS

4.1 Pure Hydrocarbons

The initial results were obtained with pure hydrocarbons. The specimens included both liquids and solids with hydrogen/carbon atomic ratios varying between zero and 2-1/3 and densities ranging from 0.665 $kg.L^{-1}$ to 2.100 $kg.L^{-1}$. Experimental values of the hydrogen/carbon atomic ratio were deduced from the DGD data using Eq. 4. The requisite attenuation cross-sections were interpolated from the tables of Storm and Israel (9). The DGD measurements are compared with the theoretical values of the hydrogen/carbon atomic ratio in Fig. 3. The agreement is surprisingly good especially considering that the attenuation cross sections may be in error by as much as 10% (9).

4.2 Heavy Oil Process Samples

The DGD method is not suited to the determination of the hydrogen/carbon atomic ratios of unrefined hydrocarbons because even very small concentrations of high atomic number elements can have an enormous influence on the attenuation ratio. However, this can be turned to advantage. In many industrial processes, including heavy oil and coal upgrading, the measurement of mineral matter and other heavy element components is of great importance. This is usually monitored by the analysis of ash which is comprised mainly of metallic oxides and silicates. One might suspect that the DGD technique could be used to monitor ash concentration.

Figure 4 shows the measured attenuation ratio versus ASTM weight percent ash for a number of heavy oil process samples. The two measurements are strongly correlated even though several different feed stocks at different operating conditions were used. For a given feed stock, the attenuation ratio correlates with the ash content to within a standard deviation of 1.3 weight percent.

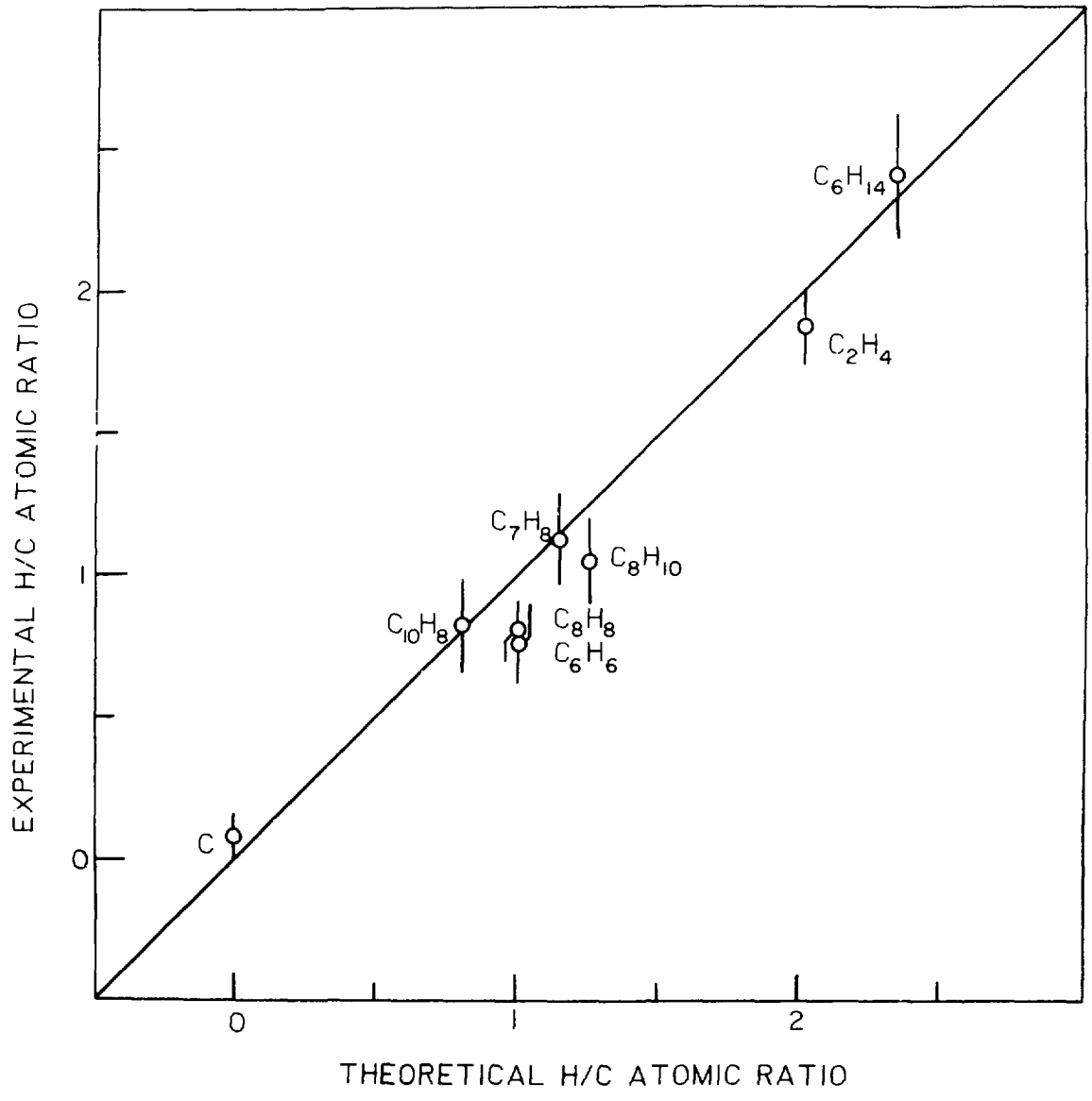

Figure 3: Comparison of theoretical values of the hydrogen/carbon atomic ratio with values measured by dual-energy gamma-ray densitometry. The chemical formulae for the specimens are recorded adjacent to the relevant data points.

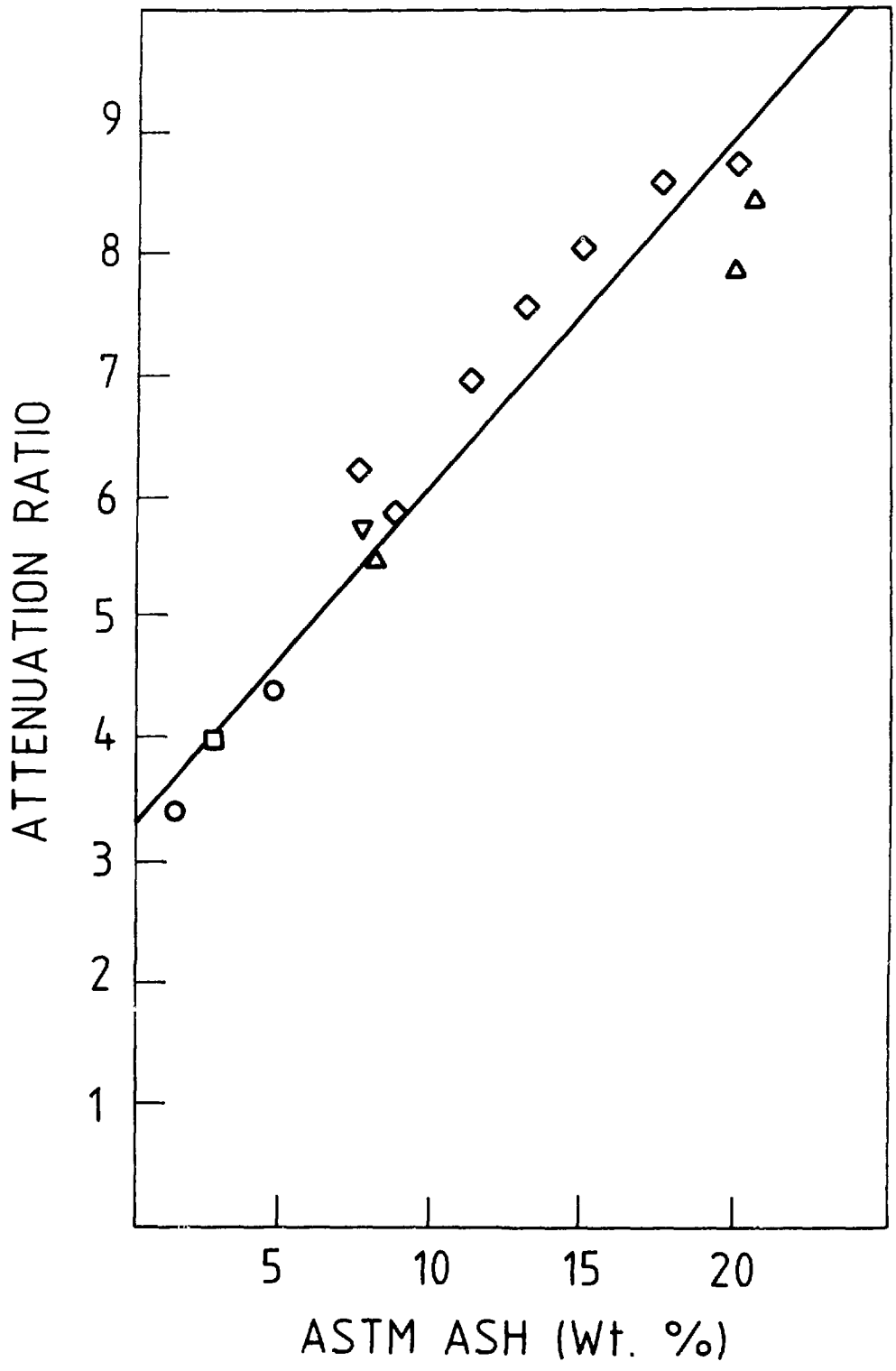

Figure 4: Measured attenuation ratio as a function of ASTM ash content. The various symbols correspond to different feed stocks.

5. DISCUSSION AND CONCLUSIONS

The measurement of hydrogen/carbon atomic ratios by the DGD method has been demonstrated for pure hydrocarbons. However, because the results are extremely sensitive to impurities, this application of the DGD technique is probably of academic interest only.

The DGD method has also been shown to be suited to the measurement of the ash concentrations of heavy oil process samples. A prototype bench-top instrument based on the present work is under construction.

The most significant feature of the DGD technique is the possibility of non-invasive on-line ash analysis. However, the thick walled steel pressure vessels required to accommodate the extreme pressures and elevated temperatures associated with direct hydrogenation processes pose a serious difficulty for the instrument engineer. Nonetheless, a DGD instrument using somewhat higher gamma-ray energies in conjunction with small thin windows is under development.

Finally, it is worth noting that the DGD method can be used to analyze any binary compound, provided that the atomic numbers of the two components are sufficiently different.

6. REFERENCES

(1) See, e.g., E.M. Goodger, "Hydrocarbon Fuels", (McMillan, London and Basingstoke, 1975).

(2) Y.T. Shah, "Reaction Engineering in Direct Coal Liquification", (Addison - Wesley, London, 1981).

(3) Y.T. Shah, "Gas - Liquid - Solid Reactor Design", (McGraw - Hill, N.Y., 1978) Ch.9.

(4) D. Adlington and E. Thompson, "Desulphurization in Fixed and Fluidized Bed Catalyst Systems", Proc. 3rd European Symp. on Chem. Reaction Eng. (Sept. 1964) p. 203.

(5) H. Fushimi, R. Kurosawa and M. Matsumoto, "Fundamental Studies on the Measurement of Coal Ash Content by the Penetration Method from Two Sources (^{241}Am - ^{137}Cs)", Prog. 8th Japan Conf. on Radioisotopes (Nov. 1967) pp. 134 - 135.

(6) R.A. Fookes, V.L. Gravitis and J.S. Watt, "Determination of Ash Content of Coal by Mass Absorption Coefficient Measurements at two X-Ray Energies", Nucl. Techniques and Mineral Resources (International Atomic Energy Agency, Vienna, 1977) pp. 167 - 182.

(7) P. Shea, R. Sher and T. Gozani, "Multienergy Gamma Densitometry: Analysis of Composite Materials", Trans. Am. Nucl. Soc. 45 (Oct. 1983) 215.

(8) R.D. Evans, "The Atomic Nucleus", (McGraw-Hill, New York, 1955).

(9) E. Storm and H.I. Israel, "Photon Cross-Sections from 1 keV to 100 MeV for Elements 1 through 100", Nucl. Data A7 (1970) 565.

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