



Optimization of a Spectrometry for Energy -Dispersive X-ray Fluorescence Analysis by X-ray Tube in Combination with Secondary Target for Multielements Determination of Sediment Samples.

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Abstract

The construction of an energy dispersive X-ray fluorescence spectrometry equipped with a conventional X-ray tube and secondary target is described. The spectrometry system constructed in our laboratory consists of a semiconductor detector system, irradiation chamber and X-ray tube. Primary source from X-ray tube was used to produce secondary X-ray from molybdenum, cadmium and stanum targets. The fluorescence X-ray from the sample was detected using Si(Li) detector with resolution of 0.175 KeV(Mn-K α). The spectrometry was used for determination of multi-elements with atomic number between 20 to 42 in river sediment samples collected from Skudai River at Johor Bahru district. The X-ray spectrums from the samples were analysed using computer software which was developed based on Marquardt method. Optimal conditions and detection limits are determined experimentally by variation of excitation parameters for each combination of secondary target, applied voltage an current of X-ray tube.

Introduction.

The application of energy dispersive x-ray fluorescence (EDXRF) spectrometry for multi-element determinations in sediment prospecting samples has the advantage of simple sample preparation, rapid analysis, good reproducibility and low cost. In this technique, primary radiation from X-ray tube are allowed to impigine on the sample, and these x-rays make photoelectric interactions in the saimple to produced characteristic X-rays. The characteristic X-rays produced are then counted by high-resolution low energy X-ray detector. However, the used of X-ray tube as primary radiation sources give a broad spectrum of bremsstrahlung together with the characteristic lines of the anode material. On direct irradiation, the primary radiation will be scattered in the sample and produce XRF spectrum with high background spectrum. Therefore, the selection of the optimal excitation energy by monochromatic X-rays is much more favourable. In this method, a beam of photons from x-ray tube will be polarized by combination of secondary target and filter to produce monochromatic radiation. The intensity of continuum radiation and scattering background from the tube will be reduced and hence improve the minimum detection limit. Since the secondary target and filter can be interchanged, hence monochromatic x-rays of different energy can be obtained by use of the same primary radiation of x-rays tube.

The present paper describes the construction of an energy dispersive X-ray spectrometry equipped with a conventional X-ray tube and secondary target, which was constructed in our laboratory. The optimization of parameters influencing detection limits is investigated. The detection limit and ranges of application for various secondary target will also be discussed in this work.

Description of the Experimental Apparatus.

The EDXRF system constructed in our laboratory is shown in Figure 1. The system consists of a primary X-ray source, irradiation chamber, detector system and data handling instruments. The primary X-ray is produced by a water-cooled X-ray tube with copper anode, type PW 2213/20 manufactured by Philips. The tube was generated by X-ray generator model PW1730 with maximum

power output of 1.5 kW. High voltage and current can be regulated in steps of 5kV and 5mA with maximum value of 100kV and 100 mA respectively. The tube has beryllium windows with 300 μ m thickness that can transmit 98% of the CuK $_{\alpha}$ radiation.

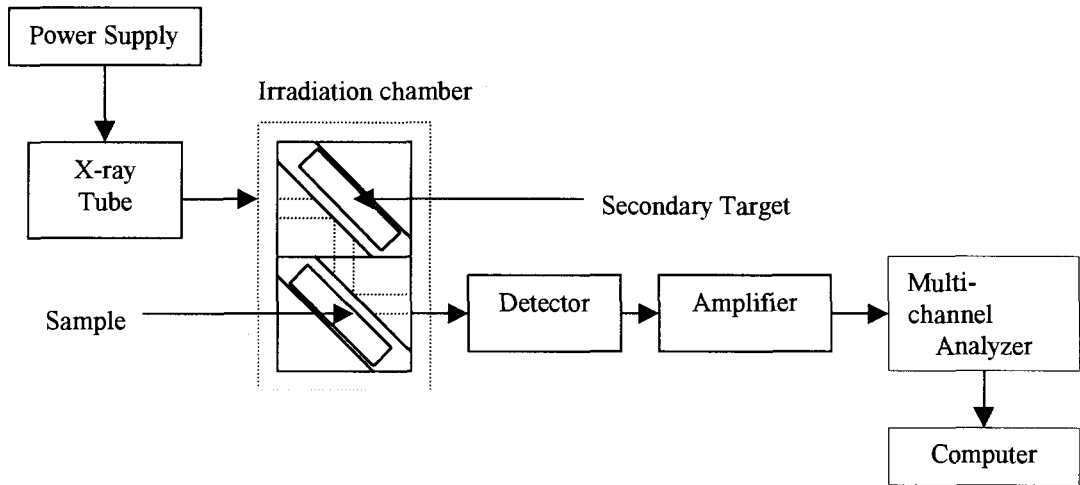


Figure 1 : Block diagram showing the arrangement of the EDXRF system

The irradiation chamber constructed in this work was made from a couple of quadratic plate of iron with inner size of 5cm x 5cm x 5cm and 1.2 cm thickness. The inner part of the chamber was covered by 3 mm thickness of aluminium plate. The secondary target was mounted in the lower part of the chamber with the position of 45° to the primary radiation (in x-direction). The sample was placed upon the upper part with the position of 45° to the secondary radiation (in y-direction). The fluorescence X-rays produced from the sample was recorded in z-direction. By using a strictly cartesian geometry in the system like this, any part of the primary radiation coherently or incoherently scattered, first by the secondary target and next by the sample, has zero intensity in the z direction. Thus, the doubly scattered radiation from the primary beam can in practice be removed from the spectrum recorded [1]. Three collimators have been mounted between the X-ray tube and the secondary target, the secondary target and the sample and the sample to the detector in order to prevent primary radiation from the X-ray tube from reaching the sample and detector directly. Block diagram of the irradiation chamber construction in this work is shown in Fig. 2.

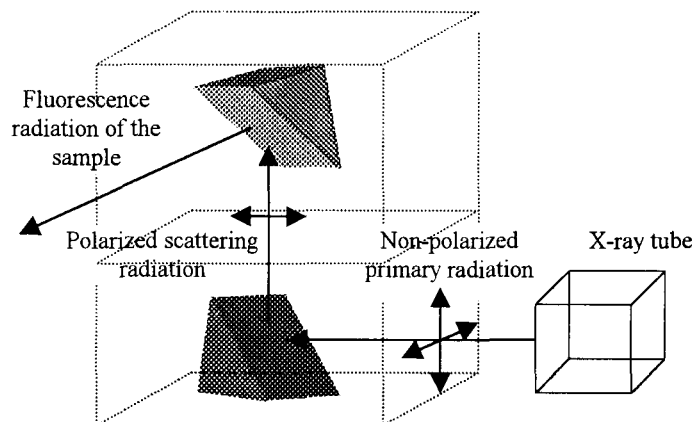


Figure 2: Block Diagram of the Cartesian excitation geometry used in this work.

The pulses of fluorescence radiation from the sample were detected by lithium-drift silicon diode detector, Si(Li). The detector has an active surface area of 28mm² with resolution of 175eV at 5.8keV (Mn-K_α). Its circular face is centered behind a beryllium entrance window with thickness of 25.4μm. The detector was cooled under liquid nitrogen temperature, 77K for optimum performance. The signal from the detector was transferred to a preamplifier (*pulsed optical feedback system*). The pulse from the preamplifier will be processed by amplifier using 10μs shaping time suitable for detection of count rate of 1000 count per second. Discrimination of pulse height will be performed by multi-channel analyzer (MCA) with 2048 channel. The "AccuSpec" software was installed into the IBM personal computer system to controlled off-line data handling.

Experiment

The sensitivity of EDXRF spectrometer depends mainly on the choice of optimal excitation conditions. In this work, the types of excitation geometry, the types of secondary targets, the high voltage and current of the X-ray tube and the thickness of the filters were optimized experimentally. In order to obtain the optimum condition of the spectrometer, the detection limits of various elements in a standardize sample were determined as a function of the parameters mentioned above. In this case a linear dependence of intensity and concentration was assumed. For the determination of the detection limit, the IUPAC definition is being used [2]. The number of counts of particular element in the sample is given by

$$N = 3\sqrt{B} \quad (1)$$

where B is the number of background counts at the peaks of interest. By considering the ratio of the element concentration and the net area of the peak is constant, the detection limit can be written as

$$C_{DL} = \frac{3C\sqrt{B}}{N} \quad (2)$$

where C is the concentration of the element in the standardize sample.

The secondary targets used in this work were molybdenum, cadmium and stannum foil with thickness of 0.0279 cm, 0.0317 cm and 0.0334 cm respectively. The thickness of the target was chosen as a critical thickness, which was calculated using the method, suggested by Tertian and Claisse [3]. The combination of applied voltage and current of the X-ray tube was set at the maximum power output. The filter used was an aluminium foil with various thicknesses between 0 to 0.9 mm.

For the purpose of optimization measurements, sample SL-1 (Lake Sediment) supply by IAEA was used. The sample was already in the form of powder of approximately 100 mesh. The sample was placed into an aluminium cup and pressed by pressing machine at pressure 10⁷ Pa for 10 minute. The thickness of the sample is about 3 mm and can be consider as a thick sample [3]. The elements investigated in this sample are Mn, Zn, As, Rb, Sr, Zr, Nb, Mo and Pb. The area under the peaks of the elements interest were calculated using computer software called 'CURFIT' which was developed based on Marquardt method [4]. The programme is capable of doing the iteration of the input data recorded by multi-channel analyzer. The minimum value of χ^2 represents the best agreement between calculated values and the experimental data.

Experimental Results.

The choice of optimum excitation geometry

In this work three types of geometrical excitation geometry were examined to obtain best detection limits of the elements interest. These are

1. Excitation in X-Y-X axis (2-plane excitation)

In this geometry arrangement, the primary X-ray from the tube will be scattered by secondary target in x-direction. Later, the characteristic line of the secondary target will excite the elements in the sample. The detector will collect the fluorescence X-rays in x-direction.

2. Excitation in X-Z-X direction (2-plane excitation)

Similar as in condition (1), but the primary X-rays from the tube will be scattered by secondary target in z- direction.

3. Excitation in X-Y-Z direction or Cartesian geometry (3-plane excitation)

In this geometry, the primary X-rays will be dispersed into 3 dimensional direction. Similar as in condition (1), but the fluorescence X-rays from the sample will be detected in z-direction.

Figure 3 shows the typical spectrum taken from the standardize sample, SL-1 using Cartesian geometry. The secondary target used was cadmium foil and applied voltage and current were set at 45 kV and 35 mA respectively. The detection limits for the elements interest were calculated and plotted as shown in Fig. 4. From the figures it was seen that the X-Y-Z excitation geometry (Cartesian geometry) always gives best detection limits compared to the others excitation geometry. This results agree with the fact that the primary radiation scattered by the secondary target and next by the sample has zero intensity in z-direction. Therefore, it was decided to used this Cartesian geometry in our EDXF spectrometry system.

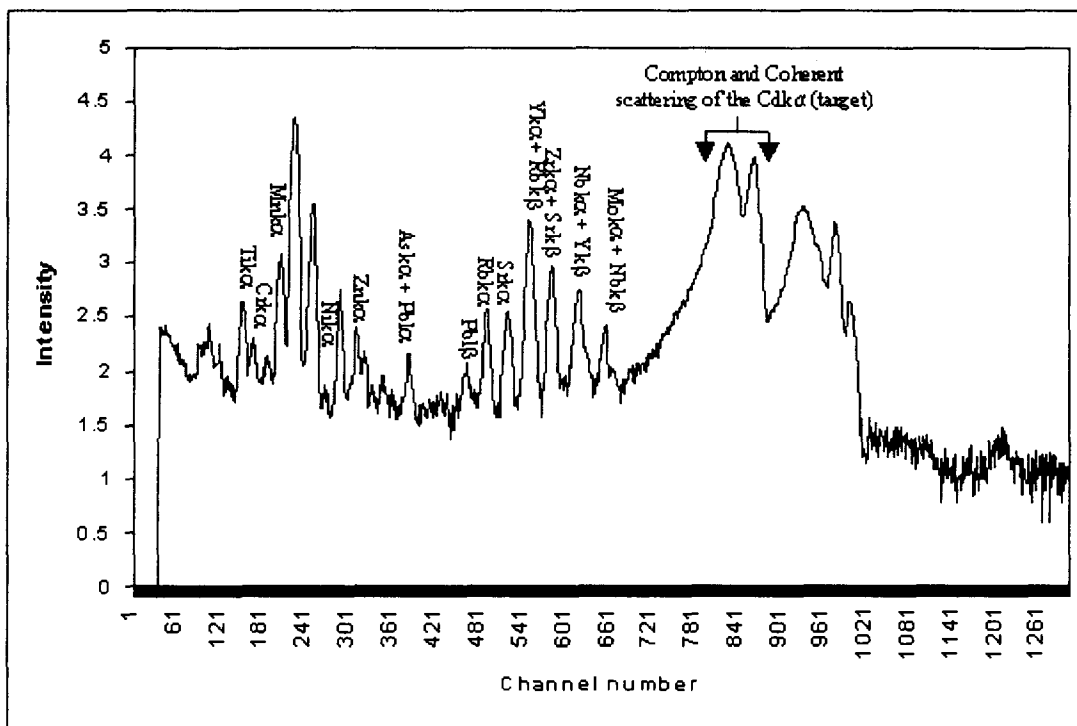


Fig 3: Typical spectrum of standard sample,SL-1 sample using Cartesian geometry.

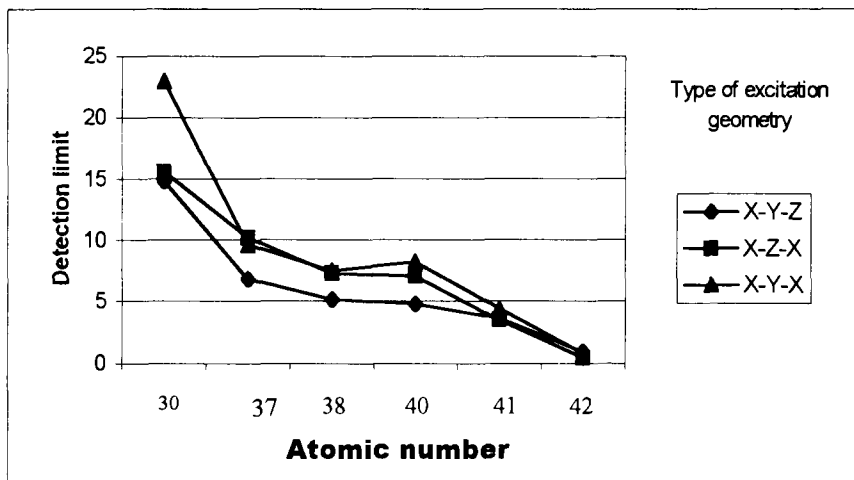


Fig 4: Variation of detection limits with atomic number for various types of excitation geometry.

Optimization of tube current and voltage.

In order to obtain the best detection limits a high intensity of exciting radiation is necessary. The intensity of the X-rays tube is given by[5]

$$I = \int_0^{\infty} I(\lambda \partial \lambda) \propto iV^2Z$$

where I is the anode current, V the anode voltage and Z the atomic number of the anode material. Because of the linear dependence of intensity on the anode current and voltage, the low detection limit can be obtained by increasing the anode current and applied voltage of the X-ray tube. The exciting radiation should be as near as possible to the adsorption edge of the secondary target material. However, as the applied voltage on the tube increase, the intensity of a lower and higher energy range will increase. Furthermore, the background will be higher due to the increasing of the scattering radiation and those increase the detection limit. On the other hand, the dead time of the electronic system increases with anode current, and the later is therefore limited by the dead time. In this work optimal values for the combination of applied voltage and current were found experimentally. Detection limits for several elements are shown in Fig 5 for difference combination set of applied voltage and current. The secondary target used in this experiment was molybdenum foil. There is no much difference in detection limits with different set of applied voltage and current for the elements with atomic number greater than 37. Therefore, any combination of applied voltage and current can be used as far as the power output reaches the maximum value.

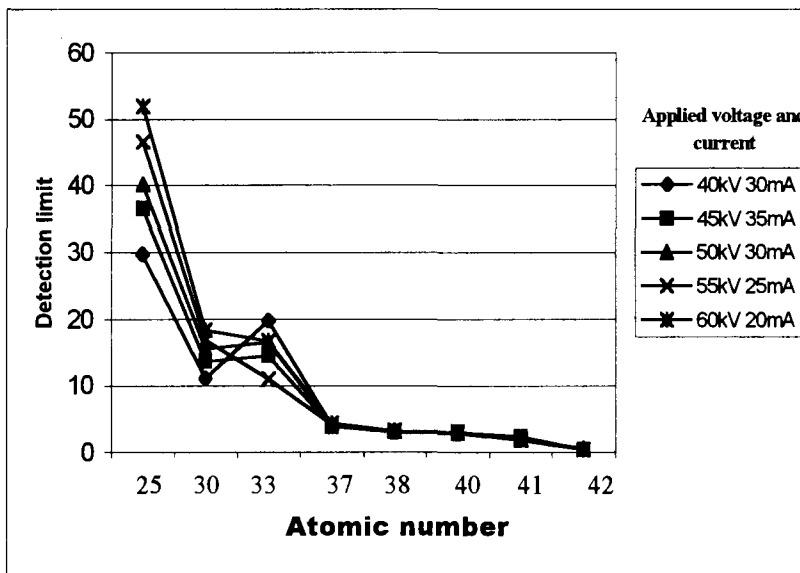


Fig. 5: The variation of the detection limits of various elements for different combinations of tube voltage and current.

The choice of secondary target

In this work, detection limits for various types of secondary target were measured experimentally. The secondary targets used were molybdenum, cadmium and stanum. For each secondary target, detection limits for various combinations of applied voltage and current were measured. Figure 6 shows the variation of minimum detection limits with atomic number of the elements in standard sample, SL-1 for three types of secondary target. From the figure, it is shown that the minimum detection limits for a particular type of secondary target decrease as the atomic number of the elements increase. This is due to the fact that the excitation efficiency of elements increases when the energy of K_{α} and K_{β} of the secondary target close to the absorption energy of the elements. It is also seen that there is no much

different in minimum detection limits for elements with $Z > 37$ for three different types of secondary target. Therefore, any type of secondary target can be used to determine the concentration of elements with $Z > 37$ in our EDXRF system. However, for elements with $Z < 37$, the used of molybdenum target will give better detection limits.

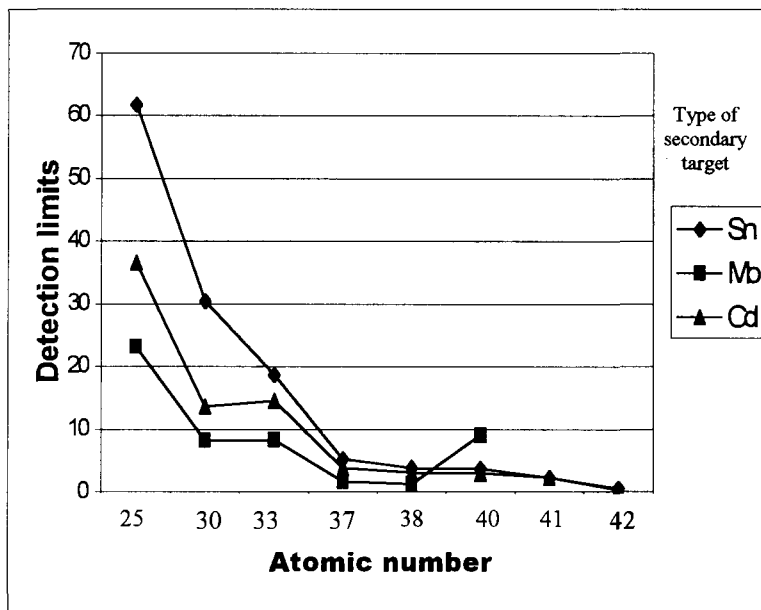


Fig. 6 Variation of detection limits (in ppm) as a function of atomic numbers for various types of secondary target.

The choice of filter thickness

In EDXRF spectrometer, filters are used in order to absorb scattered radiation containing characteristic lines and bremsstrahlung from X-ray tube. By using filters the intensity of the X-ray fluorescence from the secondary radiation is also lost. Therefore, it is important to find the optimal thickness of the filters. The filter used in this work was aluminium foil with various thicknesses between 0.3 to 0.9 mm. The filter was located between X-ray tube and the secondary target, perpendicular to the beam of primary X-rays. For a particular type of secondary target, the effect of filter thickness on the detection limits of the element of interest was measured. Applied voltage and current of the X-ray tube were set at optimum value.

Optimal conditions

The optimum parameter conditions of our EDXRF system can be obtained from the above experiments. The optimal working conditions for various elements in sample SL-1 are tabulated in Table 1.

Table 1: The optimal conditions for EDXRF system used in this work.

Type of secondary target	Applied voltage and current setting, kV, mA	Filter thickness, mm
Molybdenum	45 kV, 35 mA	0.3 mm
Cadmium	45 kV, 35 mA	0.6 mm
Stannum	55 kV, 25 mA	0.9 mm

For these conditions the detection limits for determination of trace elements in SL-1 sample by use of various secondary targets were determined experimentally. The detection limits were calculated and the results are compiled in Table 2.

Table 2: Detection limits of various elements obtained using optimal parameter conditions.

Element	Mo (ppm)	Cd (ppm)	Sn (ppm)
Mn	26.006	59.868	83.343
Zn	8.447	20.527	27.073
As	11.059	11.696	19.434
Rb	1.753	3.523	4.538
Sr	1.251	2.773	3.785
Y	0.166	0.331	0.413
Zr	6.847	2.573	3.288
Nb	-	1.559	1.916
Mo	-	0.552	0.570
Pb(*)	4.630	10.520	22.359

(*) Determination are based on the x-ray L-line

The detection limits of various elements under optimal conditions were plotted and shown in Fig 7. The results show that the used of filter can improve the detection limits of the elements with $Z > 37$. While for elements with $Z < 37$, the used of filters give a poor detection limit.

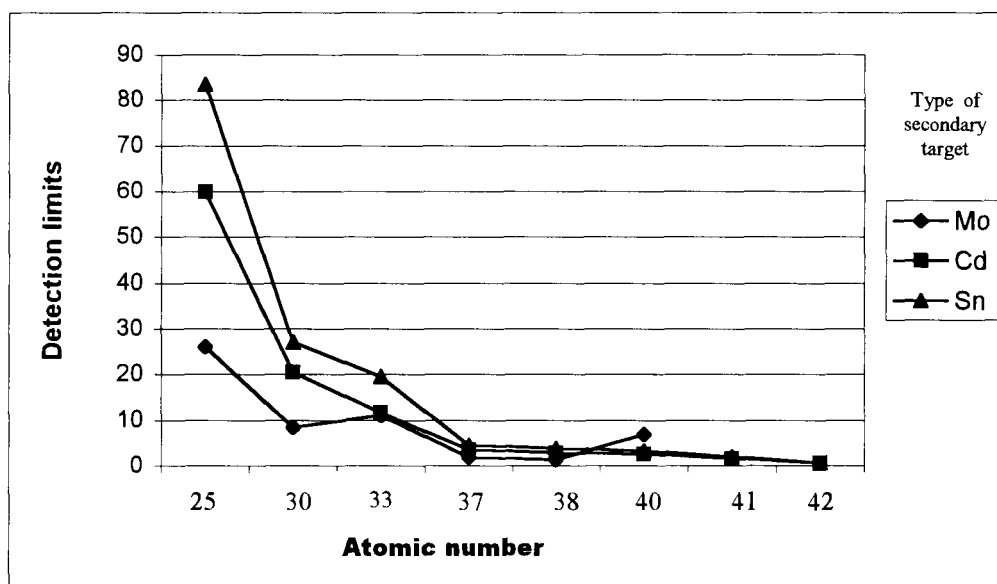


Fig 7: The minimum detection limits of element for various secondary target under the optimal condition.

Conclusion

For conclusion, the construction of EDXRF system in the work was capable of being used for multielements determination of sediment samples. The detection limits obtained in the system are reasonable and can be considered good compare than the conventional EDXRF system. The advantage of the system is simple sample preparation and rapid multielements analysis.

References:

- 1] R. Spatz and K.H Lieser, X-ray Spectrometry , Vol.8, No.3,1979,110.
- 2] Analytical Methods Committee, Recommendation for definition, estimation and use of detection limit, Analyst, Vol.12,1986,199.
- 3] Tertian R and Claisse F, Principle of Quantitative X-ray Fluorescence Analysis, Hyden and Son Ltd, London, 1982.
- 4] Hassan M, MSc Thesis, University Technology Malaysia, 1996 (*unpublished*)
- 5] R. Jenkins and J.L. de Vries, Practical X-ray Spectrometry, MacMillan, London, 1970.