Human vesical, urethral and renal stones were analyzed for the trace elements Co, Cu, Mn, Zn and Mo. Statistical correlations between the elements determined were sought which would be of possible interest in further research on the initial causes of urinary stone formation in the human body.

Introduction

Prior to the early 1960's, most studies on the elemental constituents of vesical, urethral and renal stones focused on the dietary intake and the metabolism of the bulk elements Ca, P, Na and Mg. The development of sensitive techniques like neutron activation analysis (NAA) and spark spectrometry paved the way for considering trace elements too, i.e. elements with concentrations of one part per million or less, in urinary stones and likewise in all sorts of biological specimens. Thus the Age of Aquarius unfolded with an almost universal acceptance in the fields of medical research of important correlations between trace element malfunction and human pathological states.\textsuperscript{3–5}

This research project, a continuation of a previous study by Prof. IRENEO C. LAWAS\textsuperscript{**} on the more common physical and chemical macro constituents of urinary stones, quantified the trace elements Co, Cu, Mn, Mo and Zn. Further work would include a urine survey and scanning for and quantifying of other trace elements in urinary stones — all in view of searching for clues on the initial formation of urinary stones in the human body.

Methodology

The samples were collected over a period of years and from recent patients at the Philippine General Hospital. To avoid contamination, pre-irradiation handling was restricted to homogenization of samples by powdering and then encapsulation.
in polyethylene vials. The vials were previously leached and scoured with nitric acid and rinsed with demineralized water.

The encapsulated samples, together with appropriate elemental standards, were irradiated for 8 hrs in a thermal neutron flux of approximately $10^{12} \text{n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$. Cooling for a day followed before re-irradiation in the same flux for 10 min to reactivate the short-lived isotopes.

The basic radiochemical scheme was taken from the ion-exchange chromatographic procedure developed by KRAUS and MOORE for the separation of the first transition metals in hydrochloric acid media. The samples were dissolved in concentrated nitric acid, the excess acid boiled off, and the residue redissolved in concentrated hydrochloric acid. A few drops of 30% hydrogen peroxide, added at this stage, oxidized most of the elements present to their highest valencies. This step also reduced Mn to Mn(II) and Cr to Cr(III), ionic states necessary for their successful elution in the ion-exchange scheme. The elution sequence separated the desired elements as follows:

- Cr: $12N \text{HCl}$
- Mn: $6N \text{HCl}$
- Co: $4N \text{HCl}$
- Cu: $2.5N \text{HCl}$
- Fe wash: $1N \text{HCl}$
- Zn and Cd: $0.005N \text{HCl} + \text{deionized water}$
- Mo: $2N \text{NaOH}$

Since all the counting was done with a $\gamma$-ray spectrometer, any deviation in the above separation process could easily be detected in the pulse-height distribution of the $\gamma$-ray yield from each eluted fraction.

An isotopic exchange method was developed to remove the high Na and K activities masking the Cr photopeak. The simple technique consisted in passing the sample solution through a previously equilibrated NaCl-KCl column. The separation of cadmium and zinc necessitated adsorption on another ion-exchange column of the Cd-Zn fraction in a $0.12N \text{HCl} - \text{NaCl}$ solution. Zinc was eluted from this column with $2N \text{NaOH}$ and cadmium with $1N \text{HNO}_3$. While these last two separations were easy enough, laboratory conditions precluded carrying them out on a regular basis. Samples were merely reserved for the subsequent determinations of chromium and cadmium.

### Analysis

Both samples and standards were counted by a $3'' \times 3'' \text{NaI(Tl)}$ detector connected to a 100-channel pulse-height analyzer.

COVELL’s comparator method was used in the computations for the trace element concentrations. Activities were determined by integrating corresponding photopeak areas above the half-maximum in both sample and standard gamma-ray spectra. Following CALI’s procedure, the total experimental error estimated for