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# Ancient TL

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"The empiricist . . . thinks he believes only what he sees, but he is much better at believing than at seeing."

George Santayana

IN THIS ISSUE . . .



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# INTERLABORATORY STUDY OF POTASSIUM CONTENTS USING GAMMA SPECTROMETRIC AND ATOMIC ABSORPTION ANALYSES AND COMPARISON WITH GRAIN SIZE

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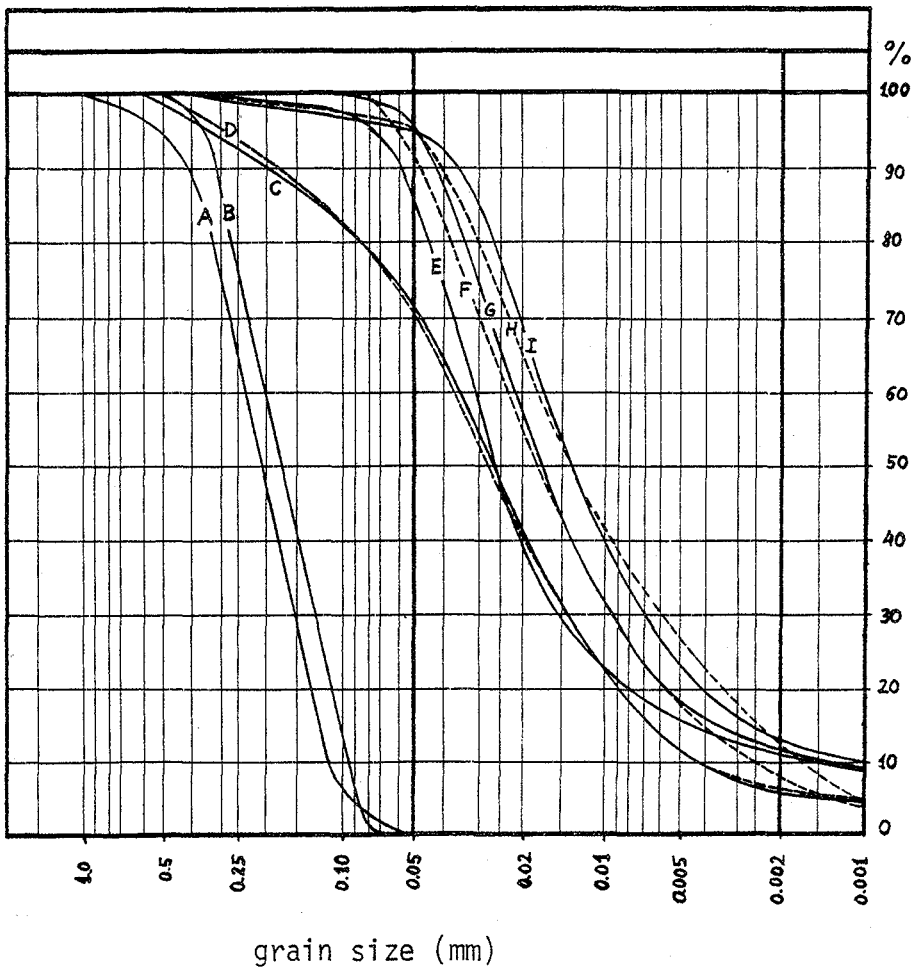
## Introduction

As part of an exchange sponsored by the Royal Society, sediment samples from Poland, which are being used in a TL dating study, had their potassium contents analysed by two different techniques. All the samples were sediments of Scandinavian origin, reworked into sands, A and B, and loesses C,D,E,F,G,H and I. The grain size analyses of each of these sediments are given in Figure 1. For TL dating an accurate determination of the potassium content is essential since the potassium content of the bulk sample is responsible for about 40% of the total dose rate to the fine grain minerals which are used for dating.

Figure 1



Gamma Spectrometry

Gamma spectrometry was carried out in the University of Warsaw using a NaI(Tl) SKG-1 detector made by Tesla-Czechoslovakia, an EMI photomultiplier tube type 9514S and a multichannel analyser type AI-1024 made in the Soviet Union. Drift was corrected by use of Co-60 peaks (1.17 and 1.33 Mev). The detector is calibrated using a standard with 3 % K (3.62% $K_2O$). The 500gram standard is made up of 28.6 gram of KCl in chemical silica. 3-5 determinations are made using a counting time of 72 minutes and two background runs each of 36 minutes are performed. Sample weight is 500 gram. The potassium window (1.39-1.57 Mev) will also contain contributions from uranium and thorium gamma decays and allowance is made for these contributions for each sample. The results are given in Table 1.

Atomic Absorption Spectrophotometry

In Cambridge the potassium contents were measured using atomic absorption spectrophotometry (AAS). These results are also given in Table 1. The error quoted is the standard deviation calculated from the number of determinations made on each sample (figure in brackets). Each determination was made on approximately 0.1 gram of sample weighed directly into a platinum crucible. 10ml of hydrofluoric acid and 1ml 50% sulphuric acid were added and the whole evaporated to dryness on a sandbath. The resulting residue was then dissolved in de-ionised water and washed into volumetric flasks. The $K_2O$ calibration solutions were made up with Analar KCl and both the standards and the samples contained 200 ppm Na to eliminate the effect of ionisation enhancement during AAS.

Discussion

The results in Table 1 are arranged in order of decreasing grain size. It can be seen that for these sediments the amount of potassium is closely connected with the granulometric composition: for sands A,B $K_2O$ is 0.6-0.7 %, for sandy loesses C,D $K_2O$ is $\sim$1.5 % and for the finer loesses 1.8-2.1 %. It is especially high for those samples which contain a lot of fine grains (2-20 $\mu$m) with a higher percentage of potassium rich minerals (e.g. K-feldspars and muscovite). The percentage of colloid clay ($<$ 2 $\mu$m) seems to be relatively unimportant. This confirms the work of Borowiec who found the maximum $K_2O$ content of Polish loesses to be in the 2-5 $\mu$m grain size (Borowiec, 1970).

For the seven samples of loess the agreement was excellent, the mean ratio of the results for the two techniques being $1.01 \pm 0.03$. For samples A and B the lower precision of the AAS results was due to their inhomogeneity.

Table 1

| | | $K_2O$ % ($\gamma$) | $K_2O$ % (AAS) | |
|---|---|---|---|---|
| A | Maliniec | 0.66 ± 0.07 | 0.69 ± 0.08 | (4) |
| B | Kraków 1 | 0.61 ± 0.09 | 0.65 ± 0.06 | (2) |
| C | Kraków 3 | 1.47 ± 0.04 | 1.47 ± 0.01 | (3) |
| D | Tyszowce 6 | 1.63 ± 0.04 | 1.55 ± 0.02 | (3) |
| E | Kazimierza | 1.70 ± 0.07 | 1.77 ± 0.02 | (3) |
| F | Komarów | 2.05 ± 0.04 | 1.961± 0.001 | (3) |
| G | Tyszowce 4 | 1.92 ± 0.08 | 1.92 ± 0.007 | (3) |
| H | Kraków 6 | 2.03 ± 0.08 | 2.07 ± 0.02 | (3) |
| I | Tyszowce 2 | 1.91 ± 0.08 | 1.89 ± 0.01 | (3) |

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Acknowledgements

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# PURITY TESTING OF TL MINERAL SEPARATES BY CATHODOLUMINESCENCE

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Many TL measurements are performed on mono-mineralic powders which have been separated from the sample of interest. A familiar example is the measurement of quartz separates in the quartz inclusion method of pottery dating. In such instances, it is usually difficult to ascertain the level of purity of the mineral separate. Sample purity is extremely important, particularly when measuring TL minerals of low sensitivity such as quartz, because only a very small amount of contamination by bright TL mineral grains, such as feldspar, can result in a significant level of abherrant TL. This type of contamination can be catastrophic for several reasons. First, the contaminating minerals might exhibit anomalous fading. Second, their dosimetry may be drastically different from that of the desired mineral. And, third, the variable number of stray grains in each TL aliquot will lead to poor reproducibility.

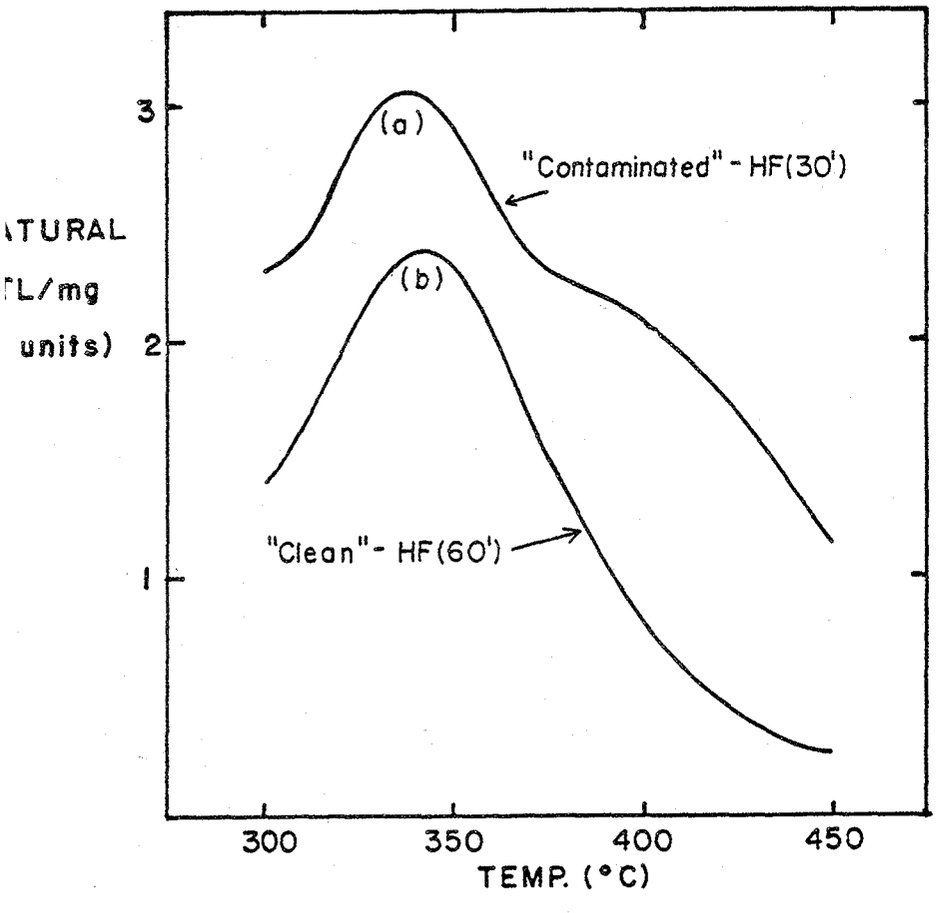
A particularly valuable and convenient tool in verifying the purity of TL mineral separates is cathodoluminescence (CL). The instrument used in our laboratory is the "Luminoscope" manufactured by Nuclide Corporation (Acton, Mass. U.S.A.). Basically, the device is a cold-cathode electron gun attached to a small vacuum chamber (roughly, 13cm x 20cm x 3cm). Samples in the form of powders, slabs or thin sections can be placed in the chamber and continuously bombarded with electrons up to 18keV (typical operating current is 0.3mA). The chamber is equipped with leaded glass windows on the top and bottom for viewing the sample and is well-suited for attachment to the stage of an optical microscope. Our particular instrument is attached to a Bausch and Lomb Stereozoom binocular microscope (with camera attachment) providing a maximum magnification of 140x.

In practice, a dozen samples can be easily loaded simultaneously. Evacuation of the chamber to about 30 microns pressure requires on the order of ten minutes and a usable beam can be obtained in as little as a few seconds. For optimum stability, the chamber should be evacuated to 10 microns and the beam maintained by dry inert gas (e.g., helium) introduced through the supplied needle valve attachment. The electron beam is focussed and centered in the microscope field of view using focusing magnets and samples are introduced to the beam by varying the position of the internal sample tray.

The excitation of mineral powders of small grain-size (<~1mm) is somewhat complicated by the tendency of the grains to charge and assume ballistic trajectories. However, we find that this is usually avoided by operating at high voltage but low current. In the case that high current is necessary to excite adequate luminescence from the sample, our standard procedure is to epoxy the grains to a microscope slide being careful not to completely cover the grains with epoxy. (This can easily be accomplished by spreading a very thin layer of epoxy on the slide with the edge of another slide, sprinkling on the grains and curing at room temperature).

An example of the usefulness of this technique is provided by some measurements performed on quartz separated from a heated granite rock from a Colorado archaeological hearth. The basic separation procedure was to soak 3mm diameter chips of the rock in concentrated HF acid to eliminate the majority of non-quartz material (principally, feldspar). After 30 minutes soaking followed by 15 minutes in aluminum chloride solution (Carriveau, Ancient TL no.1, 1977) a very clean-looking powder of white grains was obtained. Subsequent TL analysis resulted in very unreproducible weight-normalized natural TL (standard deviation of 30%). The natural TL glow curve of this material (curve a) consisted of a peak at about 340°C with a noticable bulge near 400°C. The equivalent dose curve (plateau test) also showed a bump at 400°C. CL viewing of the separate revealed the presence of a very few, bright blue feldspar grains. The level of contamination was on the order of a few grains in a 5 milligram aliquot or about 1:1000. An additional 30 minutes in the acid eliminated these grains as confirmed by CL and the reproducibility improved to 5%. In addition, the 400°C TL component disappeared (curve b) and the equivalent dose curve became more level. Obviously, the poor reproducibility resulted from the variable number of bright grains in the aliquots.

## "QUARTZ" SEPARATE GLOW CURVES




Natural TL glow curves for aliquots of 74-420 micron "quartz" powder separated from the Colorado g ite TL measured with Corning 5-60 plus 5-58 filters at a heating rate of 3°C/sec. Background negligible to 450°C.

(a) 30 minute HF soak-
CL shows contaminating bright grains.
(b) 60 minute HF soak-
CL shows clean quartz separate

Similar experiences have been encountered with quartz separates from pottery sherds. In one such case, quartz separates from Texas pottery were found to yield poor plateaus (measurements by D. Zimmerman). CL examination showed the presence of a few very bright zircon grains. Heavy liquid extraction of the zircon was required in this instance and good plateaus for the "pure" separate resulted.

Of course, this procedure prohibits subsequent use of the electron-excited grains for TL determination of archaeologic dose. In the case that sample size is limited, the CL examination can be performed on "glew" material to verify separate purity.

# 5 SPURIOUS TIDBITS

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(1) Ordinary aluminium sample discs show some spurious TL themselves and this is a serious problem with samples too thin to obscure the disc. We have eliminated this problem by cleaning the discs in hydrofluoric acid before each use as follows. After removal of grease with an organic solvent such as trichloroethylene the discs are placed in a glass beaker (~100 ml) with about 30 ml of water. About 3 ml of concentrated HF is added and stirred in; almost immediately there is considerable fizzing and the mixture becomes cloudy. After a few seconds the mixture is poured down the drain along with a large flow of water, and repeatedly rinsed with more water until the acid is all removed. We perform all these operations in a fume hood with a built-in water tap and drain.

(2) When some spurious TL is evident, but not dominant, it is tempting to subtract the reheat from the first glow to obtain the true TL. This is not the correct thing to do. The error of this method is immediately apparent if the reheat curve is higher than the first glow, as occurs on occasion. Another method of detecting this error is to stop the first glow at a lower temperature and then reheat. It is obivous that the first heating enhances the spurious signal although the mechanism for this is not known.

(3) We have for over a year now been using a model 8301 "Hydrox Purifier", sold by Matheson (P.O. Box 89, Whitby, Ontario, L1N 5R9, Canada) to remove oxygen from our high purity argon (< 5 ppm $O_2$). This has enabled us to obtain TL measurements on a number of samples with very low light levels, one as low as 20 photon counts/s, for which the TL was almost completely obscured by spurious when the purifier was not used. An example of the reduction of the spurious emission is shown in Figure 1.

Advantages of this system are its evident success and the manufacturer's statement that the purifier will easily clean the oxygen from fifty 7 $m^3$ cylinders of argon with 10 ppm $O_2$. Its theoretical capacity is 26g of oxygen or water.

Disadvantages are its high cost (~$800), it is not rechargable, it takes 30 minutes to warm up and 2 hours to cool, and argon must be kept flowing while it is warm. It cannot be used with nitrogen. Special valves and regulator are recommended for use with the purifier in order to avoid introduction of oxygen to the gas line from the air. Potential purchasers should study both the engineering report and the instruction manual before ordering in order to set up the system properly.

Another commercial purifier, model GP-100 from R.D. Mathis Co. (2840 Gundry Ave., P.O. Box 6187, California 90806 U.S.A) is available at a similar price and has the advantage of a replaceable Ti getter element and adjustable temperature; its maximum flow rate is only 1/4 ℓ/min however compared to 5 ℓ/min for the Matheson.

(4) Even with the purifier we found recently that our spurious level had been rising. We reduced it substantially by a thorough cleaning of the glow oven and using a heating tape to bake the inaccessible copper vacuum line. The problem was found after we had measured a number of samples containing organic material. It appears that such material contaminates the glow oven atmosphere and that this contamination is not removed by keeping the chamber pumped while not in use. An alternative to the cleaning that appears to work is spraying the glow oven with a silicone spray (Sil-Spray from Duxe Products, P.O. Box 1192, Cincinatti, Ohio 45201 U.S.A.) thus sealing the contaminant in place although this is only of temporary benefit.

(5) At this point two clearly separate sources of gas responsible for the spurious TL were recognized, the chamber outgassing and the argon. In order to find an optimum we tried flowing the argon through the glow oven and vacuum pump in such a way that the flow rate was 1/2 ℓ/min and pressure in the glow oven was 300 μm Hg. In this way the chamber would be continously purged and the amount of argon in the chamber would be less than 0.05% of the amount present when the chamber is at atmospheric pressure. The decrease in the spurious level was dramatic, amounting to an order of magnitude or more. An example is shown in Figure 2.

Some of these observations and developments arose as a result of severe and frustrating spurious troubles with a variety of samples. The latter included Roman pottery, Loyalty Is sherds, calcite, ocean sediments and volcanic ash samples. Despite the improvements noted we have occasionally found samples which exhibit a high degree of irreproducibility at the high temperature end of the glow curve. It is tempting to attribute this to a perhaps different form of spurious TL. We would be grateful to anyone knowing the cause or a cure if they would publicize these.

In summary, it has become apparent to us that spurious TL can be eliminated or reduced to managable proportions with straight-forward techniques. It is also clear that a vacuum system which is very "tight" and clean and which has a good pump will prevent the occurance of many of these annoyances.

The Spencer Gulf, South Australia, sample was prepared by J.R. Prescott during a visit and kindly left here for us.

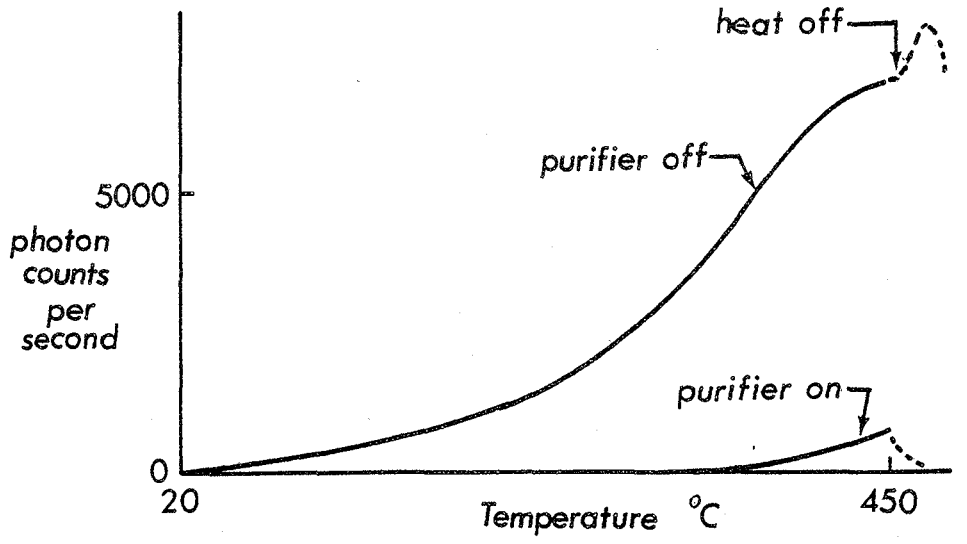


Figure 1. Demonstration of the reduction in the spurious intensity produced by the use of the Matheson purifier. The sample is Spencer Gulf sediment and has previously been glowed. The rapid increase in spurious intensity when the heat is switched off, shown in the upper curve, is curious, reproducible and unexplained.

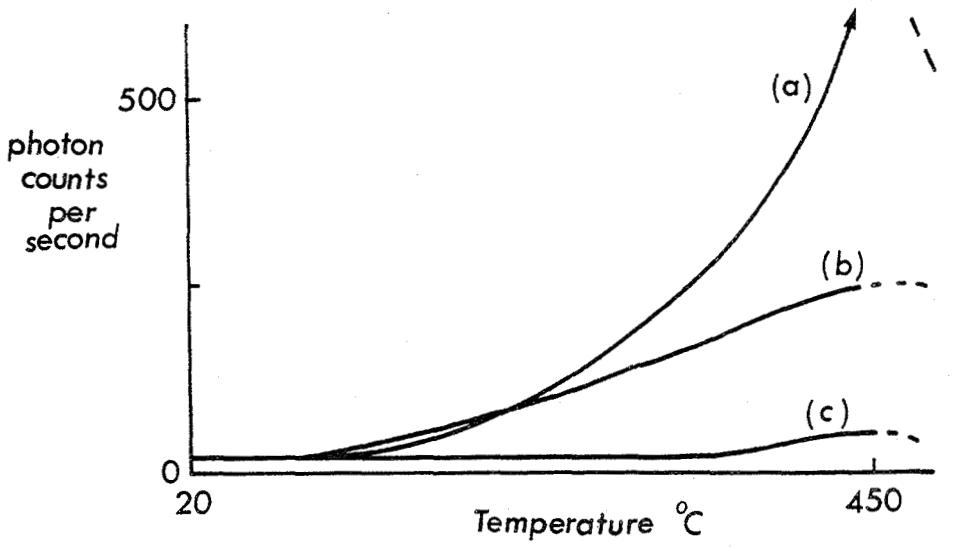


Figure 2. The same sample disc heated
a) under vacuum and being pumped
b) Ar flow 1 l/min at atmospheric pressure with the purifier on.
c) Ar flow ½ l/min at a pressure of about 300 μm Hg (not critical) with the purifier on.

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