Rhenium and Technetium Heptasulfide

We read with great interest the paper on rhenium heptasulfide (Re₂S₇) colloid by Szymendera and coworkers (1). Their characterization of the dynamics and chemical reactions involved in this synthesis is very enlightening. We hope they will do similar studies of the more popular methods of preparing Tc₂S₇ colloid using H₂S and thiosulfate. That such studies are indicated is suggested by some experiments that we did several years ago. Our preliminary investigations into the chemistry of technetium heptasulfide (Tc₂S₇) colloid preparation by the acid reduction of thiosulfate in the presence of rhenium, as described by Patton, et al (2), failed to demonstrate the formation of significant amounts of Re₂S₇. Radioautographs of paper chromatograms of several preparations (Fig. 1) indicate that the “rhenium carrier” remains primarily in the perrhenate form under the conditions of the method described by Patton. Less than 1% of the labeled rhenium remained at the point of application on paper chromatograph (Fig. 1D); it is not known if this origin material represents Re₂S₇ or perrhenate absorbed onto free sulfur. We have therefore omitted rhenium from the formula used in preparing Tc₂S₇ for liver scanning.

Under the conditions reported by Szymendera, almost all of the rhenium was bound as sulfide; this difference from our observations is probably due to different stabilizers and/or acidity in the reaction mixture from that recommended by Patton for preparing Tc₂S₇. These changes in methodology apparently are capable of producing marked changes in the yields of the various products formed. Although the variations in particle size from batch to batch with its consequent problems in interpreting the significance of its distribution has been documented (3–4), the actual chemical composition of “Tc₂S₇ colloid” obtained by various methods is not definitely known. Szymendera and his coworkers would be rendering a valuable service if they would apply their approach to the other various methods of preparing “Tc₂S₇ colloid” in the interest of clarifying this situation.

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References

The Authors’ Reply

We do appreciate Cohen and Spalter’s observation that rhenium carrier remains primarily in the perrhenate form under the conditions of Patton’s method. The point at issue is whether quite the opposite behavior of perrhenate in our technique may be due to different stabilizer and/or acidity of the reaction mixture. In this connection we have some comments.

Patton, et al have found that in the technique for preparing colloidal technetium heptasulfide without any carrier, considerable amounts of soluble technetium remain in the mixture as the result of hydrolysis of the heptasulfide. They have also found that this process is accelerated at lower pH. To protect technetium heptasulfide from hydrolysis, Patton,
et al introduce gelatin and carrier rhenium at the start of the preparation run.

We have found that stabilizers interfere with the formation of both technetium and rhenium heptasulfide; the more powerful the stabilizer the more distinct is the effect. This is why we could never obtain any reasonable yield of the colloid when polyvinylpyrrolidone was added at the start of the preparation run, and why we had to introduce that potent stabilizer at the very end, after the production of the colloid was finished (it is the buffer which contains the stabilizer) (1). At the same time, we had to decrease the concentration of hydrochloric acid added to the medium to slow down the hydrolysis, occurring during the preparation run without any stabilizer.

There is also some difference in the chemical behavior of pertechnetate and perrhenate when hydrogen sulfide, either in gaseous form or split from thioacetamide or thiosulfate, is introduced into the solution. Technetium gives heptasulfide only, while rhenium yields both heptasulfide and thio-perrhenates, substituted per-salts which are more soluble than their oxygen analogues. Thio-perrhenates decompose to rhenium heptasulfide with a rate depending on pH. Hence, it is understandable that Cohen and Spalter have got almost complete yield of technetium heptasulfide (Figs. 1E and F), and only a trace output of rhenium heptasulfide (Fig. 1D).

In conclusion, we have demonstrated that in our procedure almost all the rhenium is in the form of heptasulfide. Plausibly, the reasons are as follows: (a) we do not introduce any interfering substance during the preparation run, which enables us to bring the reaction to an end for both technetium and rhenium heptasulfide; (b) we prevent hydrolysis of the colloid by working at higher pH; (c) we protect the produced colloid from deterioration by simultaneously stabilizing it with pvp and increasing pH to about 6.

We do not intend at present to follow Cohen and Spalter’s suggestion that we investigate alternative methods of preparing technetium heptasulfide colloid.

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REFERENCES

TEMPORARY CIRCULATORY ARREST IN THE EXTREMITIES TO RESTRICT DISTRIBUTION OF I.V. ISOPTES

Most gamma-emitting isotopes are administered intravenously with the intention of mapping their subsequent localization in some specific region such as brain, pancreas, kidney, etc. If it is not bound to plasma proteins, the isotope is largely lost from blood to the extracellular fluid of all tissues (except brain) within 2–3 min and regional concentration is very slow thereafter. With the circulation to all four extremities intact during these first 2 min a substantial fraction of the dose (perhaps ½) distributes to the legs and arms and serves no function in the visualization of specific organs. This loss wastes isotope and unnecessarily radiates the extremities.

I wish to suggest that sphygmomanometer cuffs could be placed high on all four extremities and interconnected by rubber tubing to a common pressure source. Immediately prior to injecting 99mTcO₄⁻, ⁷⁵Se-selenomethionine, or other isotopes intended to map a specific region, the three cuffs on the legs and uninjected arm would be quickly inflated above systolic pressure. The injection would be made, the needle withdrawn and 5–10 sec later the cuff on the injected arm would be connected to the other three. If brought rapidly above systolic pressure, the puncture site should not bleed significantly.

For scintillation angiography the cuffs need only be held 20–30 sec. For brain or other regional scans 2–3 min would be adequate to gain most of the advantage. After 2–3 min the cuffs could be individually deflated at 10–15-sec intervals to minimize any abrupt hemodynamic changes. The original inflation should be fairly rapid to minimize venous pooling in the extremities with an attendant drop in central circulating blood volume.

Carrying this regional circulatory restriction to an extreme, one would like to cut off, for the first few minutes, circulation to all tissues, but the target organ. This is, of course, impractical but the above suggestion seems a safe compromise which might be of use in certain studies.

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