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COMMENT ON “Intracavity OptoGalvanic Spectroscopy is not suitable for ambient level radiocarbon detection”

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Every new discovery must undergo thorough scientific scrutiny before being recognized. One important step in the process is confirmation by independent experiments. The case at hand is intracavity optogalvanic spectroscopy (ICOGS), which was first published by Murnick et al. in 2008¹, and claimed to have the potential to revolutionize rare-isotope measurements in general and those of radiocarbon in particular. However, since then, no data has been reported in any shape or form to support it. In spite of extensive efforts at the following five sites around the world, the original data still remains unconfirmed: 1) Murnick’s group at Rutgers University, 2) Professor Meijer’s group at the Energy and Sustainability Research Institute Groningen at University of Groningen, 3) Professor Lackner’s group at the Department of Earth and Environmental Engineering at Columbia University, 4) our group at the Department of Physics and Astronomy at Uppsala University, and 5) the company Planetary Emission Management Inc., Beltsville, MD, USA. On the contrary, a number of publications have seriously questioned the scientific validity of the original report²⁶.

The paper by Paul and Meijer² shows that there is no dependence of the optogalvanic signal on the concentration of $^{14}$C over a range spanning nearly 12 orders of magnitude. We have studied this paper and the corresponding comments made on it by Murnick, Lui and DeGuzman⁷. Here, we will summarize our opinion of both of them, and also present our collected view of ICOGS as a method for unambiguous radiocarbon detection.

In our view, the paper published by Paul and Meijer presents well-designed experiments, thorough discussions and substantiated conclusions. Most importantly, it fills a void in the aggregated literature on ICOGS¹⁶, namely the study of highly enriched $^{14}$CO₂ samples. Hence, it is an important contribution to the field, and well worthy of publication in Analytical Chemistry.

Now turning to the comments put forth by Murnick et al.: In their comments, they start by discrediting the attempts of Paul and Meijer to reproduce the Rutgers group’s 2008 results on radiocarbon detection with ICOGS¹. They claim that the experimental setup used by Paul and Meijer is too different from their own to compare results. However, in their paper Paul and Meijer clearly explain that they began by attempting to reproduce the results using Murnick’s own original setup. In fact, one of them, Dr. Dipayan Paul, spent 11 months on site at Rutgers working on a daily basis with Murnick’s group trying to reproduce their results. Remarkably, no support was found for the claims, and the data in reference 1 could not be reproduced. It was only after failing to reproduce the data at Rutgers that Paul and Meijer started to build their own setup, and tried to improve it in the way
described in reference 2. In fact, we have similarly tried to reproduce original data in vein\textsuperscript{3,4}, and subsequently attempted to detect radiocarbon with ICOGS using our own, improved experimental setup, again without success\textsuperscript{5,8}.

Murnick \textit{et al.} then cite their own 2008 paper saying that “the total ICOGS radiocarbon signal with natural abundance radiocarbon present has a high background component”, and that their method “is non quantitative and can only be used to test stability”\textsuperscript{7}. This is completely in contrast to what was actually published in the 2008 paper, where Murnick writes that the ICOGS method inherently offers “the sharp specificity required for isotope ratio analysis”, that the “nearest \textsuperscript{13}CO\textsubscript{2} and \textsuperscript{12}CO\textsubscript{2} lines are separated by more than 500 line widths” from the P(20) line of \textsuperscript{14}CO\textsubscript{2}, and that this reduces the non-resonant component of the background “by \textasciitilde 10 orders of magnitude”\textsuperscript{1}. Hence, Murnick’s comments indicate severe doubts in his own findings in the original publication\textsuperscript{1}.

Regarding the quantitative performance of ICOGS, Murnick wrote in 2008 that “the technique quantifies attomoles of \textsuperscript{14}C in submicrogram samples”\textsuperscript{11}, and we note that he now seems to agree that this is a completely unsubstantiated claim. Furthermore, in the most curious part of their comment to Paul and Meijer\textsuperscript{2}, Murnick \textit{et al.} postulate that the ICOGS data is unusable without “proper” background subtraction. If this were true, their previously reported data\textsuperscript{1} must, consequently, be incorrect, since no background subtraction was reported necessary to achieve its almost perfectly linear response with respect to radiocarbon content\textsuperscript{1}. Furthermore, the background subtraction method in question is a total mystery. The proposed “phase/signal vector analysis” is neither defined nor referenced and lacks scientific credibility. Using this arbitrary background subtraction, Murnick \textit{et al.} reanalyzed the raw data of Paul and Meijer and claim that the experiments presented in the reference 2 actually can be used to demonstrate the validity of ICOGS. This is in spite of their extensive criticism of the setup that produced the data.

Since the first publication of ICOGS in 2008, all independent research groups that have investigated the technique have brought forth grave concerns with ICOGS as a method for radiocarbon detection in general, and Professor Murnick’s 2008 paper in particular\textsuperscript{2,6}. Moreover, Planetary Emission Management Inc. have ended their interest in ICOGS\textsuperscript{9}, and moved on to a laser cavity ring-down method\textsuperscript{10} which in contrast to ICOGS, is now being used routinely for radiocarbon measurements within the environmental applications. An independent laboratory is now using a similar concept\textsuperscript{11} for pharmaceutical and life science applications. In the meantime, Professor Murnick and the Rutgers group have neither been able to reproduce their own experiments, nor publish any new results on ICOGS in the scientific literature. A publication in a conference proceedings in 2010 contained no new information\textsuperscript{12}, instead the same data set as in reference 1 were presented – a mere set of 4 data points of measured ICOGS signal amplitude as a function of the sample \textsuperscript{14}C concentration. They have, nevertheless, patented the technology\textsuperscript{13} and started attempts of commercialization within the National Science Foundation’s I-Corps program. Hence, such a motive should be taken into account when arbitrating the debate on the usefulness of ICOGS.

All information at hand, the collected data on ICOGS show objectively that the original claims by Murnick \textit{et al.} have no scientific validity. Not a single data point has been presented by anyone to support the reported finding in \textit{any way} since the 2008 report, this including the original authors themselves.

In spite of considerable costs and efforts by various groups around the world, the only comforting aspect of this whole process is that our scientific methodology is working and is able to sort out unsubstantiated claims from facts.
References


(9) [http://www.prweb.com/releases/2014/12/prweb12384777.htm?mc_cid=4180684afc&mc_eid=[UNIQID](9)]


