



# A New Plasma Oxidation Apparatus for Radiocarbon Dating

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## Abstract

Plasma oxidation has been pioneered by Marvin Rowe (Texas A&M University), Karen Steelman (University of Central Arkansas) and colleagues to extract organic carbon from mineral-carbon-contaminated rock art paints for radiocarbon dating. They have also proposed the method be used to extract carbon from archaeological artifacts that cannot tolerate traditional sampling methods. In this technique, a sample is exposed to a radio frequency (RF) generated oxygen plasma. Upon exposure, organic carbon is readily oxidized. Crucially, the sample temperature remains well below the decomposition temperature of carbonate and oxalate minerals, allowing the selective oxidation of organic carbon. We have constructed a plasma oxidation apparatus based on Rowe's design and are beginning to investigate this technique. Our initial objectives are to investigate the rates and products of plasma oxidation of various materials, compare plasma oxidation to more typical sample treatments for radiocarbon dating, such as acid-base-acid pretreatment and step heating, and to replicate some of Rowe *et al.*'s findings. Potential future applications for plasma oxidation in radiocarbon dating may involve exploiting the surface-active nature of the plasma oxidation reaction to investigate the carbon isotope characteristics of layered organic structures.

## Plasmas and plasma oxidation

Plasmas are aggregates of charged particles, typically ionized gases, with very high electrical conductivity. They can be generated from many gases (Figure 1). Common plasmas exist in neon signs and lightning bolts. The reactive nature of elements in a plasma means they can be used in a variety of applications such as low-temperature ashing, thin film deposition, and etching.

In a plasma, electron temperature can be several thousand °C, but the large mass difference between electrons and ions limits energy transfer between them. Ion and molecular temperature, then, can remain near ambient in a "cold" plasma, where only a small fraction of gas molecules are ionized.

A plasma can be created inside a gas-filled chamber using capacitive plates outside the chamber that are connected to a radio frequency (RF) generator. The rapidly oscillating electric field formed between the plates by the RF generator impinges upon the gas molecules within the chamber inducing plasma formation. Plasmas can also be formed by magnetic induction if the chamber is wrapped with an induction coil (inductively-coupled plasmas).

Effective energy transfer from the RF generator to gas molecules within the chamber requires that plasma chamber impedance be matched to that of the generator. Without impedance matching, RF power sent to the chamber can be reflected back to the source. This both reduces the power transferred to the gas and risks damaging the generator. The RF generator is designed to provide its power to a load of a given impedance (typically 50 Ω). In our apparatus, the plasma chamber impedance is much lower than 50 Ω and varies between runs. This load mismatch is rectified by placing an impedance matching network between the RF power supply and plasma chamber (Figure 2). A matching network is an adjustable device, consisting of capacitors and inductors, that can be tuned to make the total load fed by the RF power supply equal the expected load.

Plasma oxidation is a technique that uses a cold oxygen plasma to oxidize organic carbon from the surface of a sample placed in the plasma chamber. Plasma oxidation operates at low temperature (samples reach temperatures of approximately 100 °C). Such low temperatures do not affect mineral carbon (e.g. that contained in carbonates or oxalates; this C is liberated at temperatures over 600 °C). Because plasma oxidation does not affect carbonate or oxalate contaminants, samples oxidized in a cold oxygen plasma do not require acid pretreatment to remove these minerals.

A cold oxygen plasma contains several components (e.g. atomic O, metastable molecular O<sub>2</sub><sup>\*</sup>, ions O<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>-</sup>, and free electrons e<sup>-</sup>), which are reactive with materials and surfaces exposed to the plasma. Previous studies have shown that atomic O, as opposed to the charged oxygen species, is responsible for most surface oxidation within an oxygen plasma (Dai *et al.* 1995).

## Applications

Past applications of plasma oxidation to radiocarbon dating have involved dating rock art paint (see Rowe 2001) and "non-destructive" (in reality minimally or invisibly destructive) radiocarbon dating and stable isotope analyses of entire artifacts (Steelman 2004). Additional potential applications for plasma oxidation in archaeology include extracting carbon from paint on or organic matter within prehistoric plaster, or removing surficial organic contaminants from marble artifacts for analysis. Another avenue for plasma oxidation research involves investigating its utility as a surface-active technique, possibly allowing isotopic analyses or dating of very thin layers on artifacts, such as layered cooking residues on pots, or organic accretions on man-made or natural surfaces, such as soil layers on cave roots or buildings.

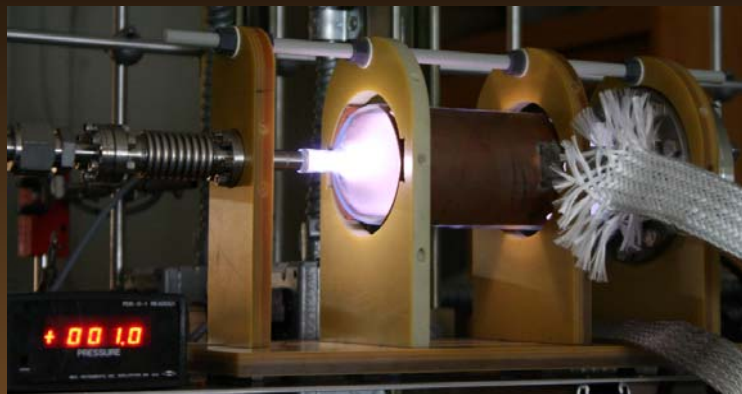


Figure 1. a 1 Torr argon plasma induced by 100 W capacitively-coupled RF power

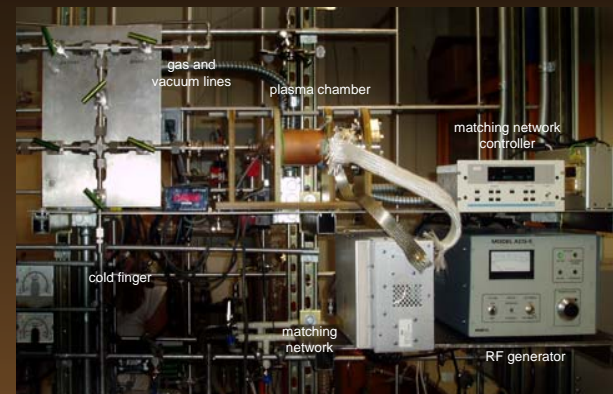


Figure 2. the NSF-Arizona AMS Facility plasma oxidation apparatus

## Equipment and methods

Our plasma oxidation apparatus (Figure 2) was inspired by the designs of Russ *et al.* (1990, 1992). It consists of a Pyrex reaction chamber, copper electrodes and leads, an RF generator and associated electronics, and stainless steel gas and vacuum lines. The electrodes capacitively couple the supplied RF power to the chamber contents. Our reaction chamber has a cold (disconnected) capacitance of 54 pF. An ENI ACG-5 RF generator, ENI MWH-5 matching network, and ENI RFC-5MW matching network controller provide 13.56 MHz RF power to the chamber electrodes by means of a pair of timed braided copper leads 1 inch across.

The ENI matching network and matching network controller incorporated in our setup (Figure 3) have replaced the manual tuning used by Rowe *et al.* When RF power is sent to the plasma chamber, the matching network controller monitors the reflected power level and varies the capacitance of capacitors C1 and C2 within the matching network in order to minimize energy loss. Automating the iterative process of impedance matching between the RF generator and the plasma chamber at the beginning of each run dramatically reduces instrument setup and tuning time.

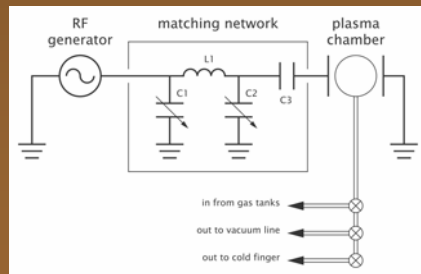


Figure 3. electrical schematic diagram of plasma oxidation apparatus highlighting the matching network

## Sample processing

1. the sample is admitted to the chamber under positive argon pressure
2. the chamber is evacuated
3. the chamber is filled with 1 Torr ultra-high purity oxygen and isolated
4. RF power is applied to the electrodes at a selected power and duration
5. the gas in the chamber is frozen into a liquid-nitrogen-cooled cold finger
6. the sample is purified and analyzed for its <sup>δ13C</sup> and <sup>14C</sup> content using standard procedures

Our plasma oxidation apparatus has just come online. We are currently testing and calibrating the operation of the apparatus, as well as verifying that 1) plasma oxidation rates of organic carbon are orders of magnitude greater than those of mineral (carbonate or oxalate) carbon, and 2) plasma oxidation does not significantly fractionate carbon.

The first test run, for example, used a mixture of 7.24 mg powdered charcoal (Rio Frio charcoal, <sup>δ13C</sup> = -23.6‰) and 12.37 mg powdered Iceland spar calcite (<sup>δ13C</sup> = +2.3‰) (both <sup>14C</sup> dead) placed in a ceramic crucible as sample material. Repeated plasma oxidations were performed on this sample, with the produced CO<sub>2</sub> recovered for analysis after each oxidation run, followed by purging the reaction chamber and admitting a fresh aliquot of 1 Torr oxygen. The results of this run are shown in Table 1.

Table 1. run parameters for plasma oxidation of a mixture of wood charcoal and Iceland spar calcite, highlighting yield and <sup>δ13C</sup> of resulting CO<sub>2</sub>

sample number	gas	power (W)	duration (min)	C yield (μg)	<sup>δ13C</sup> (‰ ±1.0‰)
KJ7	1 Torr O <sub>2</sub>	100	60	552	-22.7
KJ8	1 Torr O <sub>2</sub>	100	30	319	-22.3
KJ9	1 Torr O <sub>2</sub>	100	30	270	-23.1
KJ10	1 Torr O <sub>2</sub>	100	15	186	-24.9
KJ11	1 Torr O <sub>2</sub>	100	120	444	-22.9
KJ13	1 Torr O <sub>2</sub>	100	30	186	-24.6

## Planned research

In the near term, we plan to characterize the spectrum of gases liberated during the reaction. We suspect that CO may be generated by the oxygen plasma and plan to modify the system to include a CO to CO<sub>2</sub> conversion step.

After characterizing the basic performance of our apparatus, we plan to investigate relative oxidation rates of different classes of organic materials, the nature of the reaction on layered organic structures, and its performance in the oxidation of complex organic samples such as soil organic matter.

## Conclusions

Plasma oxidation is a technique that has previously been applied to radiocarbon dating only by the Rowe research group, using a custom-built plasma chamber and matching network. Our work thus far has demonstrated that plasma oxidation is a technique that can be performed using commercial off-the-shelf electronics with a minimum of modification. The ENI MWH-5 was modified using instructions and parts supplied by ENI to allow it to tune to nearly all capacitive plasma chambers (L1 and C3 in Figure 3 were modified from the factory configuration). This shows that plasma oxidation is a technique within the range of research groups without deep knowledge of electronics and RF power.

We look forward to working with other laboratories to characterize plasma oxidation reactions, replicate the Rowe group's previously unreplicated research, and determine what archaeological and chronometric research problems can best benefit from this technique.

## References

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