Guidelines for Use of Hydrofluoric (HF) Acid on the *JOIDES Resolution*

IODP-JRSO Managers voted on 4 October 2018 to accept the joint recommendations of the Geology and the Geochemistry & Microbiology Lab Working Groups as formal guidelines for the use of HF on the *JOIDES Resolution*. Those recommendations are given below.

Geology and Geochemistry/Microbiology Lab Working Groups: Recommendations on JRSO HF Policy

20 September 2018

The use of hydrofluoric acid (HF) on the *JOIDES Resolution* (JR) for the processing of palynological samples creates distinctive safety issues. The necessary shipboard precautions are complex and time consuming, and the shipping, transportation, storage, and disposal of HF presents additional challenges. There are also instances related to ship position, winds, and sea state that are prohibitive to the use of HF.

Community input was requested through a survey circulated to recent/upcoming participants of JR expeditions and other identified experts in the field. The survey included a list of non-HF alternatives for palynological processing and asked the community about their familiarity with these methods, positive/negative aspects of each method, environments where these methods are effective/inefficient, and the potential for unidentified methods. There was reasonable consensus that safer methods are needed, however, due to the effectiveness of HF in shore laboratories, most of these methods have not been extensively tested on IODP relevant sediments. Several environments were identified as likely to have significant processing issues with non-HF methods which included silica rich/organic poor, Antarctic sediments, and recent (Pleistocene) sediments.

The Geology and Geochemistry/Microbiology Lab Working Groups therefore make the following recommendations for the future use of HF and non-HF methods onboard the JR.

1) Non-HF methods should be used whenever possible.

To allow for proper planning, determination of the need for HF during an expedition should be made as early as possible. This includes conversations with co-chiefs at the pre-cruise meeting, as well as ongoing review during the staffing process. The Technical & Analytical Services Department has been provided with a list of Non-HF Alternative Methods (see below: ***Non-HF Methods for Palynological Processing***).

2) Limited amounts of HF will be available by request, with conditions.

If HF is requested for use on an expedition, evidence shall be provided that HF palynological processing is necessary for drilling decisions. The requestor will also provide a rationale why non-HF methods would be considered ineffective and a plan of use for HF that limits quantities as much as possible and cannot exceed 10 liters. Requests from the science party to use HF during an expedition should be evaluated by the EPM, co-chiefs, and Technical & Analytical Services.

3) Non-HF methods should be investigated and refined.

In response to the community survey, several laboratories have made offers to assist with the development of the procedures for the JR. Frida Hoem's laboratory is willing to test some of these methods on core catcher material from the Ross Sea. Sophie Warny (The Center for Excellence in Palynology - CENEX) has suggested a one-day IODP workshop in conjunction with the Palynological Society (AASP-TPS) Annual Conference in May 2020. Follow-up on both of these options is recommended.

Non-HF Methods for Palynological Processing

1) Non-acid, sodium hexametaphosphate [$(NaPO_3)_6$]
(Riding and Kyffin-Hughes, 2011, 2006, 2004)

2) Non-acid, hydrogen peroxide (H_2O_2)
(Riding and Kyffin-Hughes, 2011; Riding et al., 2007)

3) "Modified Eble" (HCl, HNO_3)
(O'Keefe and Eble, 2012; Eble et al., 1994)

4) "New Heard" technique (HClO, KOH, $ZnCl_2$)
(O'Keefe and Eble, 2012)

5) KOH processing
(O'Keefe and Eble, 2012; Hower et al., 1990)

6) Modified non-acid, hydrogen peroxide (H_2O_2)
(O'Keefe and Eble, 2012)

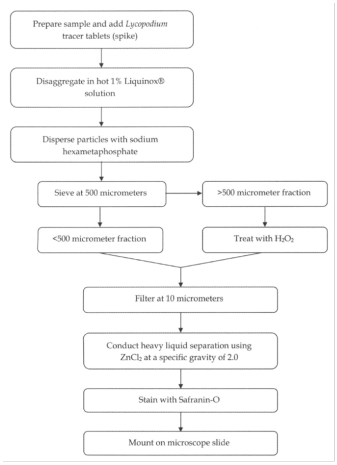
7) refined "O'Keefe" technique (HCl, Liquinox)
(O'Keefe and Eble, 2012; Van Ness et al., 2017)

8) Dense media separation (sodium polytungstate): "Campbell SPT" technique
(Campbell et al., 2016)

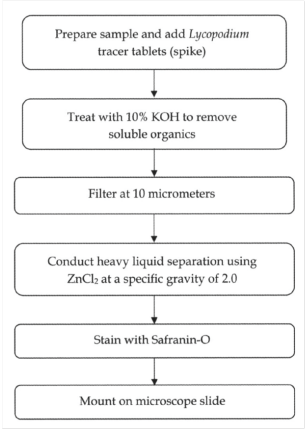
9) IODP Expedition 339 (Mediterranean Outflow)
- sieving through 100 µm mesh (discard coarse material)
- treated first with cold and then with warm HCl (30%) (remove carbonates)
- residue sieved again through a 10 µm mesh using a magnetic agitator plate (eliminate clay and fine silt particles)
- apply watch-glass procedure

Comments from sailing palynologist:
- palynomorphs in the slides less concentrated and more difficult to detect because silicate material was not destroyed by the HF
- watch-glass procedure seemed less efficient than dense media separation
- future expeditions: use both micro-sieving and $ZnCl_2$ to better concentrate the palynomorphs by eliminating the quartz particles

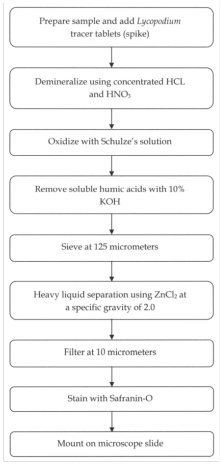
Flow Charts of Non-HF Methods



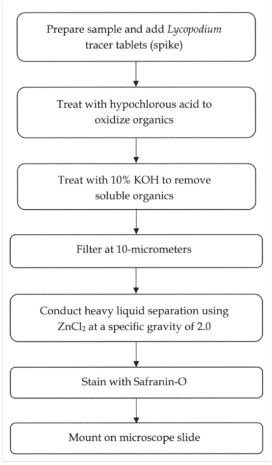
Riding-Kyffin-Hughes (H_2O_2)



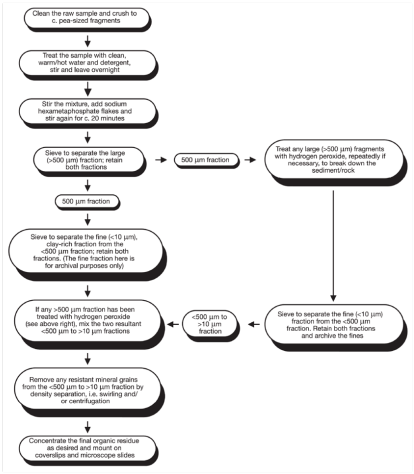
KOH processing technique



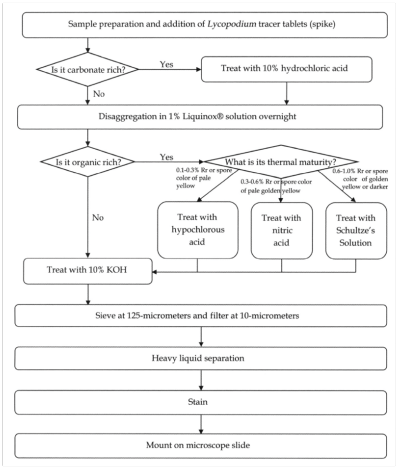
Modified Eble technique



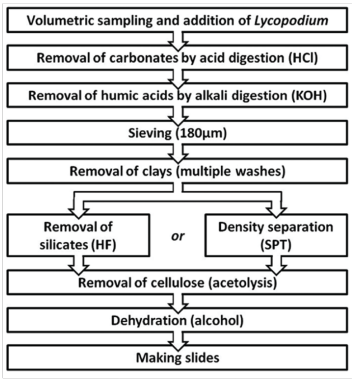
New Heard technique



Riding-Kyffin-Hughes [$(NaPO_3)_6$]



refined O'Keefe technique



Campbell SPT

Positive/Negative Aspects of Non-HF Methods

Method	Positive	Negative
Riding-Kyffin-Hughes [(NaPO3)6]	disaggregating clays, siliciclastic rocks	
Riding-Kyffin-Hughes (H2O2)		silica rich/organic poor, oxidation
Modified Eble (HCl, HNO3)	carbonates, pyrite	silica rich/organic poor
New Heard (HClO, KOH, ZnCl2)		silica rich/organic poor, environmentally unfriendly
KOH processing	lignites	silica rich/organic poor, anything not a lignite
refined O'Keefe (HCl, Liquinox)		
Campbell dense media (SPT)	environmentally friendly	

Small Volume HF Method for Palynological Processing

Enclosed microwave digestion apparatus

> "This used a relatively small volume of HF, and the vapours and waste reagent were neutralised. The method was successfully used in all 3 CRP expeditions to process a large number of samples."
> (Simes and Wrenn, 1998)

Citations:

Campbell, J.F.E., Fletcher, W.J., Hughes, P.D., and Shuttleworth, E.L., 2016, A comparison of pollen extraction methods confirms dense-media separation as a reliable method of pollen preparation: Journal of Quaternary Science, v. 31, p. 631–640, doi: 10.1002/jqs.2886.

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Hower, J.C., Rich, F.J., Williams, D.A., Bland, A.E., and Fiene, F.L., 1990, Cretaceous and Eocene lignite deposits, Jackson Purchase, Kentucky: International Journal of Coal Geology, v. 16, p. 239–254, doi: 10.1016/0166-5162(90)90053-2.

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Simes, J., and Wrenn, J., 1998, Palynologic Processing in Antarctica: Terra Antartica, v. 5, p. 549–552.