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13. ABSTRACT (Maximum 200 words)

Analytical equipment for spatially resolved composition mapping in the electron microscope has been purchased in accordance with the originally proposed intent of the grant. A scanning beam attachment for scanning transmission electron microscopy (STEM) has been acquired as well as attachments for composition mapping utilizing characteristic X-ray signals (EDS) and electron energy loss signals (Gatan Imaging Filter).

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INSTRUMENTATION FOR SPATIALLY RESOLVED COMPOSITION MAPPING IN THE ELECTRON MICROSCOPE

FINAL REPORT

Samuel P. Gido

December 11, 1995

U. S. Army Research Office

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The aim of this one year instrumentation acquisition grant has been achieved in that we have purchased analytical equipment for spatially resolved composition mapping in the transmission electron microscope (TEM). As originally proposed, we were to add a scanning attachment to our existing 200 kV TEM to make it a fully functional STEM. Additionally we were to acquire energy dispersive X-ray spectroscopy (EDS) and parallel electron energy loss spectroscopy (PEELS) for this instrument. The 200 kV STEM with EDS and PEELS would provide the proposed composition mapping capability. We were very fortunate, however, because in addition to this DURIP grant we also secured two other major instrumentation grants this past year: 1) An NSF grant for two SEM's equipped with their own EDS systems, and 2) a W. M. Keck Foundation grant for a 300 kV TEM. The success of these two other grants led us to propose some modifications to the equipment list proposed for the DURIP grant. We were able to use our considerable purchasing power with electron microscope and analytical equipment manufactures to obtain a higher level of instrumentation for the same price as originally quoted in the DURIP proposal. Attached to this report is a copy of a letter to the program director explaining these changes, and how they would further enhance the capabilities discussed in the original DURIP proposal. A copy of the program director's return letter granting permission to make these changes is also attached.

The changes in the instrumentation purchases are as follows:

1. The proposed analytical components were acquired for the new Keck funded 300 kV TEM rather than our old 200 kV TEM. The 300 kV instrument is a JEOL 3010. With DURIP funding we acquired scanning capability (STEM) and EDS for this instrument.

2. Instead of purchasing a PEELS system for the 200 kV TEM (as originally proposed), we purchased a Gatan imaging filter (GIF) system for the new 300 kV instrument. As discussed in more detail in the attached letter to the program director, the GIF is a new type of instrument which collects the same electron energy loss signal as the PEELS but does so in a more rapid and efficient way. The speed of data collection is very important for work on electron beam sensitive polymer materials.

In order to get the best deal from the instrument vendors we combined the procurement of all new instrumentation from DURIP, NSF and the Keck Foundation into one master RFP which was put out for competitive bidding. The sections of this purchase were, however, divided to keep instrumentation funded by different sources separate. A copy of the introduction to the overall bid specifications is attached to this report. Item II (Analytical Components for TEM) was the part funded by this DURIP grant. The detailed specification under item II are also given. The detailed specifications for the other components of the overall package which were not funded by DURIP are omitted from this report but are available upon request. The competitive bidding process was won by a partnership of three firms with JEOL of Peabody, Massachusetts supplying the electron microscopes, Princeton Gamma Tech of Princeton, New Jersey supplying the EDS systems and Gatan Inc. of Pittsburgh, Pennsylvania supplying the GIF. Orders were placed on July 29, 1995.

In conformance with these specification the equipment purchased with DURIP funds includes:

1. ASID for JEM 3010 (Beam Scanning Unit for 300 kV TEM): $ 100,000

2. Princeton Gamma Tech 60 mm^2 EDS detector with computer and software for digital composition mapping: $35,000.

3. Gatan 678-3K/10B (Gatan Imaging Filter): $165,000

This equipment was provided with a 1 year warranty. The total cost is $300,000, of which 50% was paid by the University of Massachusetts as match to the $150,000 provided by the DURIP grant.

As of the date of this report, the new equipment purchased on the DURIP grant in being delivered as set up along with the other electron microscopy and analytical components which we purchased from other grants. Although the new equipment is not fully operational and has thus not yet been formally accepted by the University, we have managed to get useful data from the equipment on the silk protein research projects which were discussed in the DURIP proposal. Thus two recently submitted manuscripts, one to *Macromolecules* and one to *Science*, acknowledge the support of this DURIP grant.

1. Regina Valluzzi, Samuel P. Gido, Weiping Zhang, Wayne S. Muller, and David L. Kaplan, "A Trigonal Crystal Structure of *Bombyx mori* Silk Incorporating a Threefold Helical Chain Conformation Found at the Air-Water Interface" Submitted to *Macromolecules* 12/29/95.

2. P. Jeanene Willcox, Samuel P. Gido, Wayne S. Muller, and David L. Kaplan, "Evidence of a Cholesteric Liquid Crystalline Phase in Natural Silk" Submitted to *Science* 12/8/95.

Copies of these manuscripts are included.

Since this was an instrumentation acquisition grant, no personnel were supported.

No inventions are reported for this grant.

Specifications for Electron Microscopes and Related Analytical Equipment for the Polymer Morphology Laboratory at the University of Massachusetts Amherst

The University of Massachusetts wishes to purchase an integrated package of instrumentation for electron microscopy and related analytical techniques which must include the following major components:

I. Transmission Electron Microscopes

A. Analytically configured 300 kV transmission electron microscope (TEM).

B. A 200 kV TEM configured for high resolution imaging. This 200 kV instrument may be a used or demonstration model, but it must have resolution equal to or better than our existing 200 kV TEM, a JEOL JEM 2000 FX I. It must also have more modern and reliable vacuum and computer control systems than our existing 200 kV instrument. The vendor, if they so desire, can take our JEOL JEM 2000 FX I as a trade in for the more modern replacement 200 kV TEM.

II. Analytical Components for TEM

C. Analytical components to be fitted to the 300kV TEM requested in item A. Scanning transmission electron microscopy capability (STEM), an energy dispersive X-ray spectrometer (EDS) capable of detecting light elements down to Be, and a Gatan Imaging Filter (GIF).

III. Scanning Electron Microscopes and Related Components

D. A close working distance, cold cathode, field emission gun (FEG) scanning electron microscope (SEM) for high resolution imaging and analysis of materials surfaces. This FEG SEM must additionally be equipped with EDS capable of detecting light elements down to Be.

E. A thermionic source SEM. This instrument must also be equipped with an EDS system.

F. An ion beam coater to produce ultrathin metal coatings on surfaces to be imaged at high resolution in SEM.

IV. Terms and Conditions

G. Installation and proof of resolution in our laboratories. Electron microscopes must work with their analytical components (EDS, STEM, GIF) as integrated packages.

H. User training on all new instruments.

I. A 1 year warranty covering all parts and labor on all instruments must be included.

J. Current service contract pricing information must be provided so that we can estimate our projected yearly operating costs after the warranty period is over.

K. All shipping costs and duties (if applicable) must be included in the quoted instrumentation prices.

The 200 kV TEM is the only electron microscope in this package of instrumentation which may be a used instrument; all other electron microscopes must be new. The University of Massachusetts will only consider purchase of instrument models with proven records of reliability and performance, from vendors with proven records for service and support. Thus the University will only accept bids to supply instruments for which there is at least one current customer site installation, under service agreement, in the United States.

The contract will be made to the vendor, who in our opinion, best meets our needs based on performance, price, service, reputation, conformance to specifications, and any other consideration deemed important. The University of Massachusetts Amherst reserves the right to reject any or all bids and is not necessarily bound to accept the lowest priced proposal if it is contrary to the best interests of the University.

II. Analytical Components for TEM

C. Analytical components will be supplied for the 300 kV TEM in order to make it a fully functional analytical instrument: These include (1) a beam scanning attachment to enable the 300 kV TEM to function as a scanning transmission electron microscope (STEM); (2) An energy dispersive X-ray spectrometer (EDS), and (3) a Gatan Imaging Filter (GIF).

1. A beam scanning unit must be supplied for the 300 kV TEM specified in Section A.

a. This unit will provide STEM bright field (BF) and dark field (DF) imaging capability, and secondary electron imaging (SEI).
b. STEM resolution will be 2.0 nm or better.
c. SEI resolution will be 3.0 nm or better.
d. The beam scanning unit must be useable with both ultrahigh resolution and analytical pole pieces, should we decide later to convert the instrument to the ultrahigh resolution configuration at a later date.
e. Ultra High Resolution Camera for Photography (2000 lines or better)
f. Wave form monitor.
g. Polaroid #545 film back.

2. An energy dispersive X-ray spectrometer (EDS) must be supplied for the 300 kV TEM which should include the following, components and meet the following specifications. These requirements, including an very large detector active area as well as digital electronics, are designed to maximize data collection rates thus minimizing the exposure of sensitive polymer samples to the electron beam. The EDS performance of the integrated TEM/STEM/EDS system will not be diminished during cryogenic operation.

a. <u>X-ray detector with the following characteristics and minimum requirements:</u>

* Permanent ultrathin window capable of withstanding 2 atmospheres of pressure.
* Active Area: 60 square mm. (larger than usual to facilitate high solid angle and thus high data acquisition rates)

* Interface to 300 kV TEM column with a take-off angle of 25° or more and solid angle of 0.17 Str. or more.
* Resolution 143 ev FWHM or better
* Boron Peak to valley ratio 25:1 or better
* Maximum throughput: 50,000 counts per second or better
* C, B resolution: 85 eV or better
* Retractable

b. Computer system (may be demo unit):
* Work station performance.
* 17" color monitor or larger
* minimum of 16 MB RAM
* minimum of 500 GB hard disk
* Tape drive, and 3.5" floppy drive
* Ethernet compatible
* Files must be exportable over network or disk to both PC and Macintosh systems

c. Data Acquisition Hardware (for maximum collection speed):
* Digital pulse processing electronics, to eliminate analog electronics including amplifier and ADC to improve resolution , count rate, and light element sensitivity.
* Throughput rates exceeding 50,000 counts per second with zero peak shift

d. Analysis Software:
* X-ray processing software for automatic identification of peaks and analysis of spectra.
* Quantitative Analysis Software including light element quantitative analysis.

e. Microscope digital beam control integration:
* Image signal processor for digital scan control of STEM.
* Image and digital map collection:
  Collection of 1024x1024 pixel images or maps
  Collection of at least 10 X-ray map and an image signal simultaneously
* Display of 1024 x 1024 pixel image at full resolution
* Computer controlled electron beam positioning
* X-ray analysis of selected points of displayed digital image.
* Interactive mouse control of beam to position location of desired analysis.
* Can analyze multiple points, and can automate analysis of a number of points distributed across a use defined line or grid.
* Collection of X-ray data with static or scanning beam.

f. Color Printer output of images and X-ray composition maps
* Tektronics Dye Sublimation Printer 220 E or equivalent (may be demo unit).
* Hewlett Packard Laser Jet 4 Printer with 300 dots per inch or better resolution.

3. Gatan Imaging Filter (GIF) for electron energy loss signal filtering must be supplied for the 300 kV TEM: Gatan model GIF200, Gatan part number 678-3K/10B. We require the parallel signal processing of the GIF which provides electron energy loss data on the entire image at one time. A digital parallel electron energy loss spectrometer (PEELS) which builds up the compositional map pixel by pixel with a scanned focused probe is far too slow for our applications on electron beam sensitive polymers and protein crystals.

This filter is specific for 300 kV TEM's with a Grade B 1024 x 1024 pixel CCD detector. This system is attached to the bottom flange of the TEM, and is able to form electron energy filtered images when the TEM is operated in the imaging mode. When the TEM is operated in diffraction mode, the GIF must be able to perform energy filtering on electron diffraction patterns. The GIF must also be capable of acquiring electron energy loss spectra.

The images and spectra should be viewed in real time on a pneumatically retractable TV-rate camera. It must then be possible to capture images and spectra using a built in slow scan CCD camera. The images and the spectra must be free of all 1st and 2nd order aberrations and distortions permitting collection angles as high as 100 milliradians to be used for spectroscopy.

This system must include computers and any additional electronics and software required for the control of the instrument, the collection of images and spectra, the analysis and display of this data, and the storage of a large number of images and spectra. This system should be able to interface with the color printer specified above in the EDS section in order to print out images and spectra.