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PIXE AND SEM STUDIES OF OLD FINNISH AND EUROPEAN GLASS AND EUROPEAN OYSTER *Ostrea edulis*

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Abstract

Proton induced X-ray emission (PIXE) and scanning electron microscopy (SEM) with an energy-dispersive spectrometer (EDS) and wavelength-dispersive spectrometer (WDS) have been used to determine elemental concentrations in old Finnish and European glass samples.
A comparison of the SEM and PIXE methods based on the measurement of reference glasses also shows that in analysing major and minor elements of old lead glass samples the WDS results are comparable to those obtained using the EDS method. The accuracies of WDS measurements of Ti, Mn, Fe, Zn, Cu, and Ba with concentrations at 0.5 wt% WDS are comparable to values obtained for PIXE, but precisions are 20-40 % while in the PIXE measurements they are under 10 % with the exception of Ti. At the level of 0.05 wt% the precisions are about 10 % and accuracies 20 % in the PIXE measurements, while in the WDS measurements they are 20-50 % and 40-80 %. The exceptions are the accuracies for Ti and Mn, which are 1 % and 11 % and thus more comparable to the approximately 20 % values of the PIXE measurements.
Shells have been used as a source of lime in ancient times. The possible impurity elements originating from the use of ancient shells of European oyster, *Ostrea edulis*, are manganese, iron, zinc bromine and strontium. If 1/10 of the lime has been introduced into the glassmaking mixture as shells, then the concentrations of iron and strontium elements are detectable on the ppm level. If the whole amount of lime needed in glass production has been added as shells, then the concentrations of manganese, iron, zinc, bromine and strontium are detectable on the ppm level. Analysis of the nacreous layer of *Ostrea edulis* shell samples from a period spanning 4200 radiocarbon years was performed using the PIXE method. The Mn/Ca, Fe/Ca and Pb/Ca ratios were higher in the recent shells.

CONTENTS

1 Introduction

The findings reported in this thesis are based on the use of proton and electron beams in the analysis of old Finnish and European glass and European oyster *Ostrea edulis*. The quantitative information on the major, minor and trace elements of archeological artefacts, including glass, is important in resolving problems connected with manufacturing technology, raw materials, the origin of these objects and their restoration and protective conservation. Many kinds of techniques have been used to analyse glass composition including wet chemical analysis [1], atomic absorption spectroscopy [2-4], neutron activation analysis [5-6], inductively coupled plasma atomic emission [7-8], and X-ray fluorescence [9]. The analytical methods used in this study, scanning electron microscopy (SEM) using both energy-dispersive (ED) and wavelength dispersive (WD) spectrometers and the proton induced x-ray emission (PIXE) method, are based on detection of characteristic X-rays. Shells were used as a source of lime in glass making in ancient times [10]. Therefore the elemental composition analyses of shells are interesting from the point of view of research of old glass. In addition, sells are important pollution indicators.

Glass is one of the oldest artificial materials known to man. Glazed steatite and faience objects were made in northern Mesopotamia in the fifth millenium BC. The oldest recipes for glazes are in the Babylonian chemical text of 1700 BC and the oldest recipes and processes of glass making are recorded on clay tablets from the Royal Library of Assur-bani-pal in the seventh century BC. Silica, lime and alkali are basic components of oxide glasses, which are of greatest importance both historically and technologically. The source of silica was sand. The question

of lime is an interesting one. Three ancient literary references (the Babylonian chemical text, the Niniveh tablets and Pliny in the first century A.D. speaks of shells) mention lime as a constituent of glass. Then there is no reference to lime for sixteen centuries. However the content of lime is from five to twelve percent in ancient glasses, and in medieval glasses sometimes exceeds twenty per cent [11]. Turner shows very convincingly by means of analyses that lime was not deliberately added but was instead added as constituent of sand and/or alkali [12]. Up until the medieval period in both Western Europe and the Near East, the dominant alkali in ancient glass was soda originating from natural deposits or salts obtained by deliberate evaporation of sea or river water. The other major source of alkali was marine plant ash. During the medieval period (up to 100 AD), more readily available sources of alkali came to be used, such as ashes of trees (oak, beech, and birch) and bracken, which have high potassium contents. The glass that resulted, known as Waldglas (forest glass) in German areas, was a potash glass. The early production of the first Finnish glass factories was this type of glass.

The aims of this thesis were to study how the PIXE and SEM methods suit the needs of glass research. Due to its flexible network structure glass can include more than half of the elements of the periodic table. Due to this several methods are needed in elemental composition analyses of glass. The advantages of SEM-EDS and SEM-WDS techniques include the small size of the samples (< 1 mm^3) needed and the ability to analyse corroded samples. On the other hand, there are limitations to these methods. They have poor sensitivity to trace elements and to elements lighter than Na. The sensitivity of the PIXE method at the trace element

level is significantly better than the sensitivity when the atomic number Z of the detected element is in the region 18-40. A disadvantage of the PIXE method is that the light elements (Na, Al, Mg, Si) important in glass research cannot be detected. Studies using EDS for glass analysis have been published [13-14] and the problem of analysing ancient glasses with WDS have been discussed in previous works [15-16]. The PIXE method has been used in analysis of archaeological material including glass [17-19]. Because glassworks in different areas used local raw materials, it is presumed that the chemical composition of the glass varied from one area to another or even from one factory to another. Therefore, it might be possible to determine where a piece of a particular glass was manufactured on the basis of its chemical composition. Trace element concentration is a ”fingerprint” of the factory. Accuracy, precision and detection limits of three different methods (SEM-WDS, SEM-EDS and PIXE) were compared in the analyses of old glass samples.

In the oyster research, the main aims were to investigate differences between the chemical concentration ratios in the nacreous layer of shells of the European oyster, *Ostrea edulis*, from the period spanning about 4200 radiocarbon years, and to get information about the temporal history of pollution. The PIXE technique was used to determine the ratios of Sr/Ca, Mn/Ca, Fe/Ca, Zn/Ca, Br/Ca and Pb/Ca in oyster shell samples collected from three different sites on the coast of Ireland. Information about the trace elements or impurity elements which could originate from shells if they have been used as a source of lime in glass production is valuable for the research of old glass.

This thesis includes the following publications**:**

This thesis includes the following publications**:**

I P. Kuisma-Kursula, J. Räisänen, E. Spring and H. Matiskainen: Proton-induced X-ray emission analysis of early Finnish ”Waldglas”, *Glastech. Ber.*, **64** (1991) 137-140.

II P. Kuisma-Kursula, J. Räisänen and J. Donner: PIXE-method determination of the elemental composition of the European oyster Ostrea edulis, *Nucl. Instr. Meth. Phys. Res.*, B **95** (1995) 523-526.

III P. Kuisma-Kursula, J. Räisänen and H. Matiskainen: Chemical analyses of European forest glass, *J. Glass Studies* **39** (1997) 57-68.

IV P. Kuisma-Kursula and J. Räisänen: Scanning electron microscopy-energy dispersive spectrometry and proton induced X-ray emission analyses of medieval glass from Koroinen (Finland), *Archaeom.*, **41**, 1 (1999), 71-79.

V P. Kuisma-Kursula: Accauracy, precision and detection limits of SEM-WDS, SEM-EDS and PIXE in the multi-elemental analysis of medieval glass, *X-Ray Spectrom.*, special issue (in press).

VI P. Kuisma-Kursula: Bromine in the medieval glass samples from the museum Aboa vetus in Turku (submitted for publication in *Glastech. Ber.*).

These papers will be referred to in the text using Roman numerals I-VI. In all papers the external PIXE method was used in trace element analyses. In papers III and IV, major and minor elements of glass samples were determined using the SEM-EDS method. In paper V major, minor and trace elements were measured using the SEM-WDS method. Paper I analyses Finnish potash glass from the 19^{th} century. Paper II measures trace element ratios in the nacreous layer of the European oyster, *Ostrea edulis*. Paper III analyses European potash glass from ten different sites. Paper IV presents the elemental composition of potash, soda and lead glass from Koroinen, the area where the first large modern archaeological excavation in the history of Finland took place, between 1898 and 1902. Paper V is a study of accuracy, precision and detection limits of SEM-WDS, SEM-EDS and PIXE methods. Paper VI is a study of bromine as a ”fingerprint” element in medieval glass from the museum Aboa vetus in Turku.

2 STRUCTURE AND PROPERTIES OF GLASS

2.1. Structure of glass

Glass is made by heating together ingredients at a very high temperature to form a liquid, then cooling this liquid to room temperature. Through cooling no discontinuous changes take place in the glass melt; it gets stiffer and stiffer until it is rigid like a solid, yet maintains the internal structure of a liquid. In a liquid the atoms are joined to one other in a random structure rather than a regular extended three-dimensional pattern.

The major constituent of most common glass is silicon dioxide (silica), SiO_2, derived from ordinary sand. In its crystalline form its basic structure is that of a tetrahedron, with four oxygen atoms surrounding a central silicon atom. In the early 1930s W. Zachariasen [20] calculated forming energies of the crystalline form and the glass form of silica and showed them to be close to one other. On the basis of his calculation, he concluded that the glassy silica is composed of the same structural parts as the crystalline silica and developed the random network model. This remains the foundations for modern research on the structure of the glassy state.

The major raw materials of the most common commercial glasses are the same as the oldest known glass recipe on the Assyrian clay tablet from the Royal Library at Nineveh: sand, limestone and soda. The soda acts as flux and the limestone as a stabilising agent to form a durable glass. Ancient glasses are also frequently of this soda-lime-silica composition. The other major type that is found is potash-lime-silica glass, where potash replaces the soda as the fluxing agent. Lead lowers the melting temperature of glass. Its use has a very long history [21]. Studies of the first literary references and first uses of specific elements in glass making have been published [12]. Comparisons have been done between the composition of medieval glass and the account of Theophilus, whose writings (De Diversis Artibus) represent our most important contemporary source on the technology of glassworking in medieval Europe [13, 22].

2.2. Colour in glass

Colourlessness is apparently the most common property of modern glass, even though colourless glass only became popular in the 17th and 18th century when the use of glass windows became more prevalent. In ancient times glass was a material for jewels and ornaments, and colour was its most desirable property.

Common glass is colourless because there are no such electronic states of atoms or molecules which could absorb visible light. Light can pass through the glass virtually unhindered. Small amounts of impurities in the glass batch like iron, copper and cobalt, give intensive colours to glass. The most important glass colorants belong to the first transition series (Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn) because for these atoms the energy of visible light (E=1.77-3.10 eV) quanta is high enough to eject outer orbital electrons and light is thus absorbed. In addition to absorption, colours in glass can be produced by light scattering. The actual colour produced by a colorant depends on the environment of the particular colouring ion in the glass and especially on the oxygen potential of the glass. Many colours are therefore sensitive to the furnace atmosphere where the glass is made [23, 24].

Because of a lack of chemical knowledge the old glassmakers could not identify colouring agents uniquely. They used the same name for different substances and different names for the same substance. Therefore the information contained in glass recipes and accounts over the centuries is difficult to understand. However it is assumed that colouring element like iron, manganese, copper and cobalt were familiar to old glassmakers [14] even though many colours of medieval potash glass were produced using only iron and manganese [25].

2.3. Corrosion

Glass is quite resistant to corrosion, but it can suffer corrosive attacks when it is placed in contact with water (as may be the case at an archaeological site or in a

damp atmosphere). This is because the water leaches out alkali, sodium or potassium from the surface. Knowledge of the structure and composition of corrosion layer(s) is valuable for restoration and protective conservation strategies of old glass objects. The other reason for world-wide attention to corrosion studies of glass is the decision, taken by several countries, to immoblise high-level nuclear waste by vitrifying it. The safe disposal of nuclear waste evidently calls for a clear understanding of the factors which govern the aqueous corrosion of glass. Many studies have been written on corrosion of glass due to air [26-28] and due to soil [29]. Even corroded samples about 2000 years old have been analysed [30].

3 Structure of oyster ***Ostrea edulis***

The shell of *Ostrea edulis* consists of three layers. The whole shell is covered by an organic layer, the periostracum. Beneath it lie two other calcified layers that are much thicker. The outer of these two layers consists of vertically arranged prisms, while the inner layer is made up of the horizontal plates constituting the nacreous layer. The nacreous layer is composed of crystals of aragonite, as opposed to the prismatic layer, which consists of calcite. Both calcite and aragonite are crystalline forms of calcium carbonate [31, 32]. The structure of the shell is presented in the Figure 1 [33].

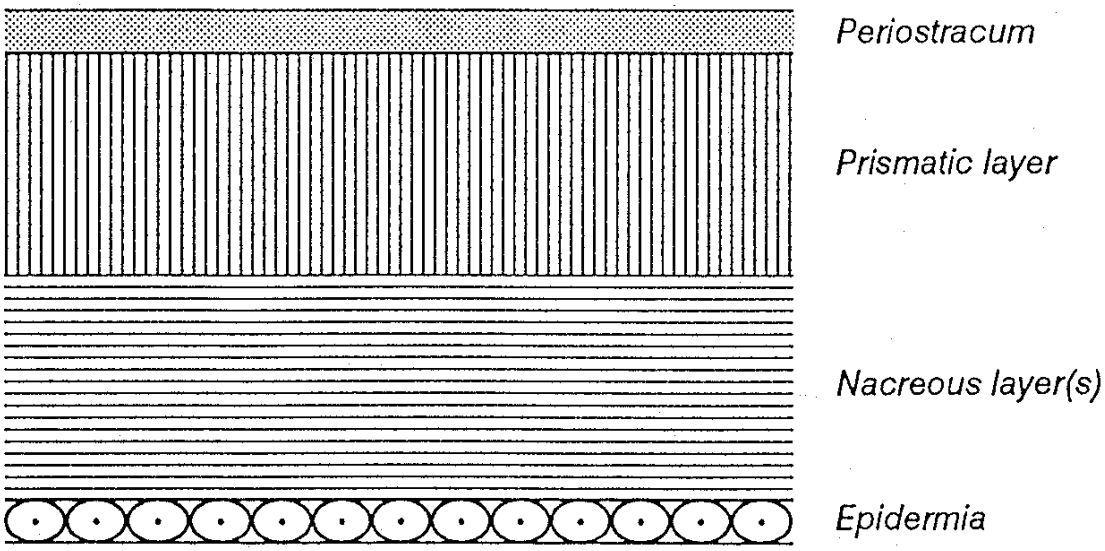

Figure 1. The structure of the shell [33].

Sea shells are composed of nearly 100 % calcium carbonate. In addition to this, many minor and trace elements can be found in varying amounts [34]. Trace element contents of shells have been shown to vary with environmental conditions such as temperature and salinity [35].

If shells have been used as a source of lime in the glass production process, then the impurities originating from this material are manganese, iron, zinc, bromide, strontium (papers II and VI) and some other elements [34]. Manganese and iron are included in other major constituents of glass, namely sand and alkali . It is unlikely that we could determine which part of each impurity originates from each raw material. In addition, concentrations of impurity elements originating from shells should be only a few ppms, at most ten even if the whole amount of lime (at the most 20 wt% of raw materials) has been added as shells. The evaluation of the absolute concentrations of calcium, manganese, iron, zinc, strontium and bromine in the oldest oyster shells of Paper II has been done using the IAEA (International Atomic Energy Agency, Vienna, Austria) animal bone standard (H-5) and presented in Paper VI. On the basis of the oyster research (Paper II) and the analyses of glass samples from the museum Aboa vetus in Turku (Paper VI), the interesting ”fingerprint” element could be bromine. Bromine could also originate from marine plants or, most probably, from salt used as an alkali source.

4 Sample preparation

4.1. Glass samples

The glass samples analysed in Paper I were from the following glassworks: Mariedal (Sipoo 1779-1824), Åvik (Somero 1748-1833), Nyby (Ii 1782-1885) in Finland and from Björknäs (near Stockholm 1736-1785) in Sweden. The samples analysed in Paper III were from ten different sites in Central Europe and Estonia. The samples analysed in Paper IV were excavated from Koroinen, near Turku.

The samples analysed in Paper VI were from the museum Aboa vetus in Turku. The location of these sites are shown in Figure 2.

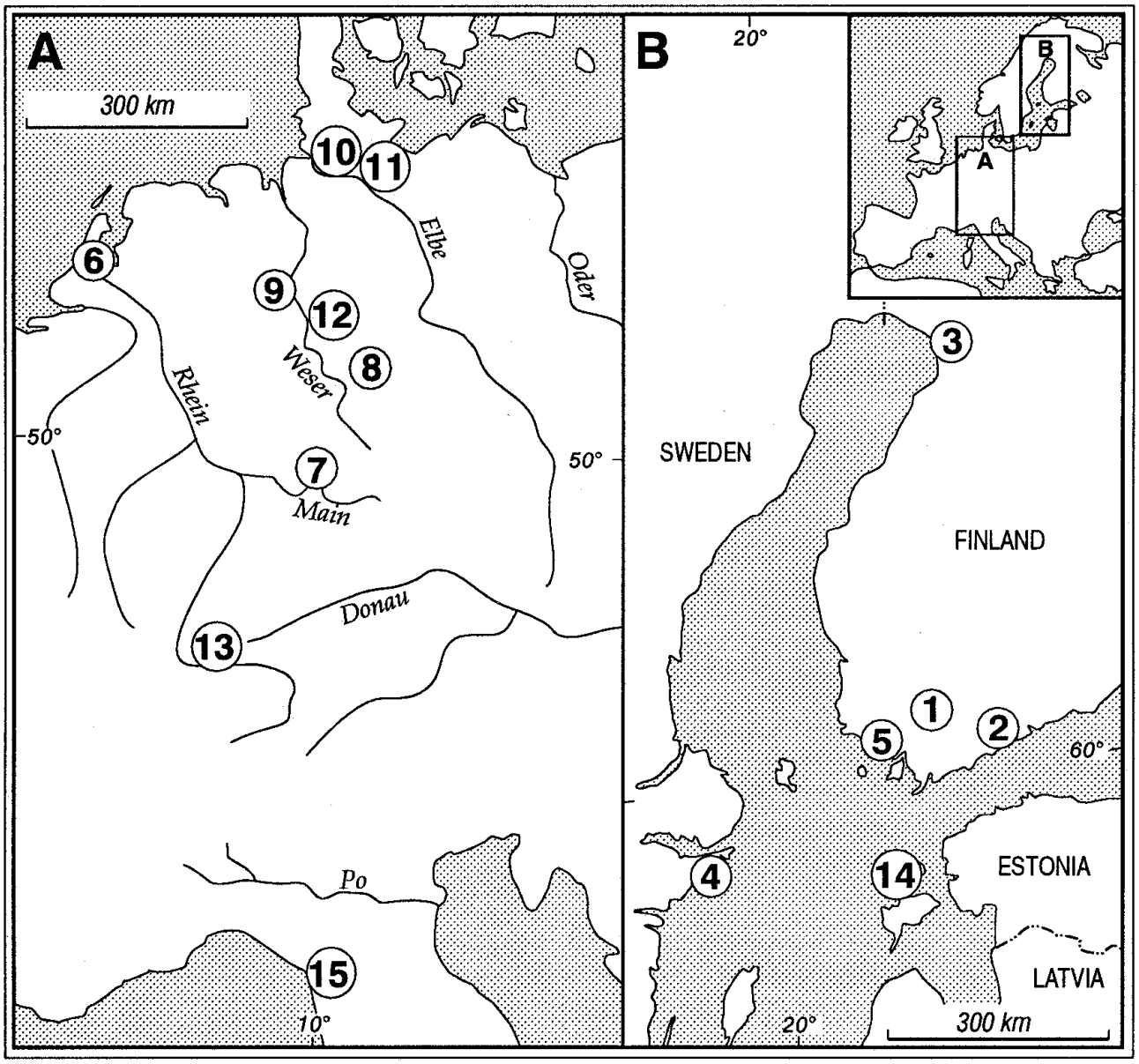

Figure 2. Location of the sites of glass samples analysed in this work: (1) Åvik, (2) Mariedal, (3) Nyby, (4) Björknäs, (5), Turku (Koroinen, Aboa vetus museum), (6) Amsterdam, (7) Spessart, (8) Kaufunger Wald, (9) Höxter, (10) Holstein, (11) Lubeck, (12) Hils, (13) Black Forest, (14) Hiiumaa, and (15) Tuscany.

The window glass fragments excavated from Koroinen are the oldest window glasses found in Finland, dating from the era prior to the fifteenth century [36]. They are emerald-green lead glass. This type of glass has not been found anywhere else in Finland. The glass vessel samples analysed are presented in Figure 3 with one lead glass vessel fragment. This glass vessel fragment consists of two parts: a yellowish one and a green one. Both parts are alkali-free lead glass. The lead glass window samples are presented in Figure 4. The numbering of the glass samples follows that presented in Paper IV.

Figure 3. The glass vessel fragments excavated from Koroinen.

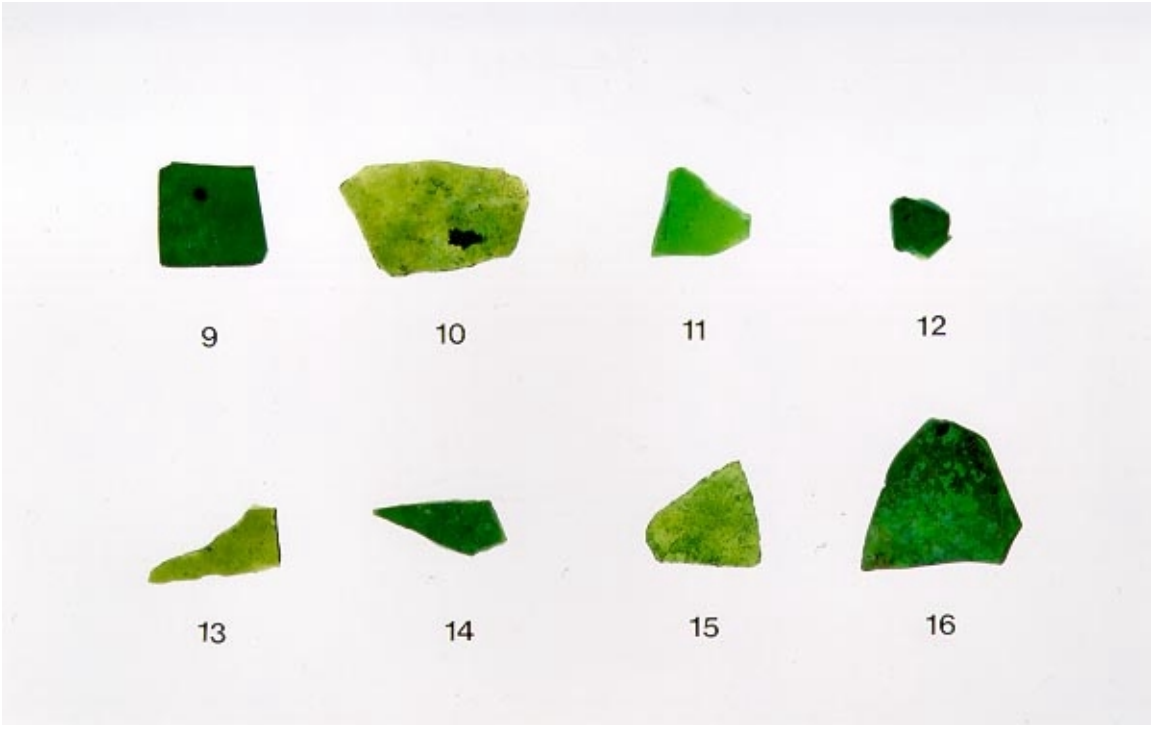

Figure 4. The lead glass window fragments excavated from Koroinen.

4.2. Glass sample preparation

Glass is usually a homogeneous material, and small area flakes are generally representative of the chemical composition of the glass artefact. Nevertheless, some precaution should be taken to make analyses really representative of the bulk glass composition. First, the analysed area must be polished before analysis. All ancient glass artefacts, even those exhibiting a glossy, well-preserved surface, are covered by modified layers whose chemical composition is completely different from that of the bulk. Second, some heterogeneities or unevenness of the surface could be present. Such areas must be excluded from the analysed area.

For the PIXE analyses in the present work the glass samples were cleaned with cerium oxide or polished with pumice. For the SEM analyses small samples were cut from the glass artefacts with a diamond saw, mounted on epoxy resin and polished flat. A carbon coating was evaporated on the polished surface to prevent localised charging and any resulting distortion or reflection of the electron beam.

4.3.Oyster sample preparation

The samples were cut with a thin diamond saw from the hardest white part of the oyster shell after the removal of the rough outer layer. The samples were collected from the following sites in Ireland: (1) Dublin, (2) Culleenamoore, and (3) Strandhill. The location of the sites where the oyster samples have been collected are presented in Figure 5.

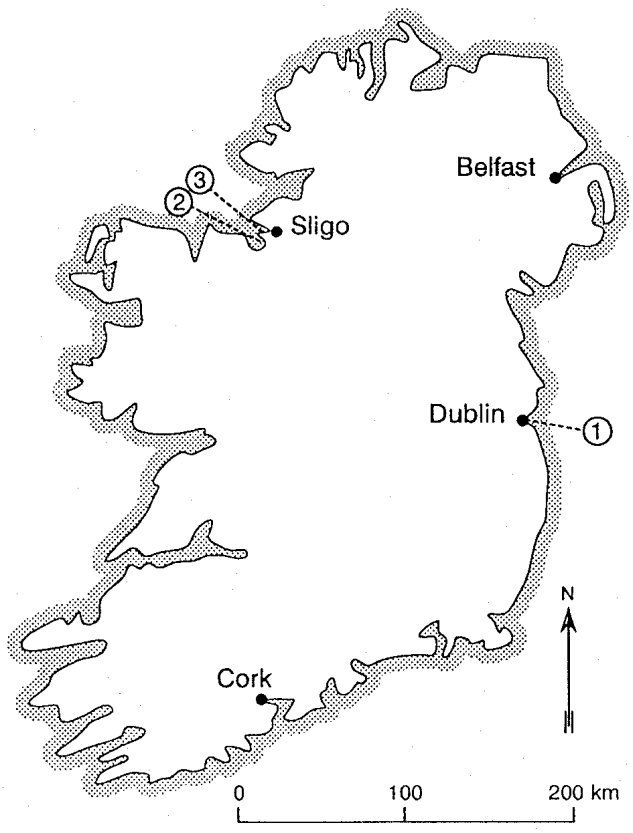

Figure 5. The location of sites of the studied oyster samples: (1) Dublin, (2) Culleenamoore, and (3) Strandhill.

5 Proton and Electron Induced X-rays

5.1. Characteristic X-rays

X-ray emission lines are produced by transitions of atomic electrons from one energy level to another. For such a transition to be possible, a vacancy must first be created by the ejection of an inner electron. The required inner level ionisation is produced by protons in the PIXE (proton induced X-ray emission) analysis and by electrons in the SEM (scanning electron microscope) technique. If the initial ionisation is in the innermost atomic shell, the resulting X-ray emission is identified as K radiation. X-ray emission is known as 'characteristic radiation' because the energy (wavelength) is specific to the emitting element. Since only inner electrons are involved, characteristic X-ray energies are practically independent of the physical and chemical state of the emitter [37].

5.2. Historical note

Characteristic X-rays were discovered in 1909 and in 1913-14 Moseley [38, 39] found that the frequency of emitted characteristic X-ray radiation is a function of the atomic number of the emitting element. This discovery led to the technique of X-ray spectrochemical analysis, by which the elements present in a specimen could be identified by the examination of the directly or indirectly excited X-ray spectra. The electron microscope was discovered in the 1930s. The idea of the electron microanalyser, in which a focused electron beam was used to excite a small area on a specimen and which included a light-optical microscope for locating the area of interest, was patented in the 1940s. In his doctoral thesis, R. Castaing [40] developed the physical theory enabling the analyst to convert measured X-ray intensities to chemical composition. Prior to the late 1960s the main detection option was wavelength-dispersive spectroscopy (based on Bragg's law). The coupling of electron microscope and microanalyser followed after the addition of the energy-dispersive detector to the electron microanalyser in 1968. X-ray excitation cross sections for protons of MeV energies are similar to those for electron beams in the 10-50 keV region, but the bremsstrahlung intensity is much smaller for protons than for electrons. The low X-ray background makes it possible to use the proton induced X-ray emission (PIXE) to measure trace element concentrations down to levels of about 1 ppm. This was observed by Birks et al. [41]. The first experiments of the PIXE technique were made by Johansson et al. in 1970 [42].

5.3. The PIXE method

5.3.1. Quantitative PIXE analysis

Characteristic X-ray intensities are proportional to concentration. In theory, X-ray yield and the concentration of an element in a homogeneous thick target are related by the following equation:

$$Y_i = nC_i\omega k\varepsilon \int_{E_0}^{0} \sigma_i(E)T_i(E)(-dE/dx)^{-1}dE, \qquad (1)$$

where
- n is the number of proton
- C_i is the concentration of element i in the target
- ω is the probability of the emission of X-rays or the fluorescence field
- k is the relative line intensity of possible transitions
- ε is the detection efficiency
- $\sigma_i(E)$ is the ionization cross section for proton energy E
- $T_i(E)$ is the transmission of photons from successive depths in the matrix
- $-dE/dx$ is the stopping power of the target for the incoming protons
- E_0 is the initial proton energy

If the ionization cross section, stopping power and attenuation coefficients are known as functions of particle energy numerical integration of equation (1) is possible but difficult, and the result is inaccurate. In practice the basis of quantitative analysis is the comparison of intensities of characteristic X-ray lines emitted by the specimen with those from reference standards [43].

5.3.2. Background

Low background radiation is the main advantage of the PIXE method over electron excitation or X-ray fluorescence (XRF), but this radiation is still not negligible. The background spectra is mainly composed of (a) bremsstrahlung from secondary electrons, (b) brremsstrahlung from the projectile and (c) gamma-rays from nuclear excited states.

(a) Bremsstrahlung due to secondary electrons

In the low energy region of a PIXE spectrum, the main source of background radiation is bremsstrahlung from secondary electrons removed from the target due to proton impacts. The maximum energy that an incident particle can give to the secondary electron is:

$$T_m = 4m_eE_p/M_p \qquad (2)$$

where m_e is the electron mass, M_p is the proton mass and E_p is the proton energy. The secondary electron bremsstrahlung spectrum is very intense below the energy of T_m but decreases rapidly at higher energies.

(b) Bremsstrahlung due to the incident projectile

This is the principal cause of background radiation in electon induced X-ray analysis. In classical terms, bremsstrahlung emitted by a decelerating particle is proportional to the square of the acceleration and thus also to $(F/m)^2$, where F is the electrostatic force on a projectile of mass *m*. Since the forces are the same but the masses differ by a factor of 1836, the primary proton bremsstrahlung should be lower in intensity by a factor of $1/(1836)^2$, or approximately $3x10^6$, than it is in the electron excitation . This difference is lessened by the fact that the proton undergoes more collisions than an electron during its passage through the target. Nevertheless, proton bremsstrahlung is very small compared to the electron case.

Projectile particle bremsstrahlung decreases with particle energy and the cross section formula contains the term $(Z_p/A_p-Z/A)^2$ where Z_p and A_p are atomic number and atomic mass of the projectile; Z and A refer to the target. This has the effect that if Z/A is the same for both the projectile and target, the bremsstrahlung yield will disappear. Protons do not fulfil this condition; proton bombardment is

always accompanied by projectile bremsstrahlung. However, it is significantly lower than in the case of electron excitation.

(c) Gamma-rays

The 2-3 MeV protons may induce nuclear reactions and produce gamma radiation. The intensity of the gamma depends on the presence of certain elements which have high gamma-ray yield (e.g. sodium, aluminum and fluorine) [43-45].

5.3.3. Detectors and filters

Although wavelength-dispersive (crystal) spectrometers have been widely used in electron induced X-ray analysis, most PIXE work has been carried out using energy dispersive Si(Li) or intrinsic Ge detectors. A good crystal spectrometer can have an energy resolution of < 10 eV, depending on the X-ray energy, which is far better than the 170 eV resolution of the intrinsic Ge detector used in the PIXE measurements of this thesis. The good resolution of the crystal spectrometer is achieved at the cost of a greatly reduced solid angle of detection and detector efficiency. In trace element analysis the absolute amount of signal is at a premium, and so detection efficiency must be maximised and a large solid angle detection, capable with energy-dispersive detectors, is preferred. The other point is that the wavelength-dispersive technique is generally limited to detecting a single element at a time. By adding more crystals and detectors three or four elements may be detected simultaneously. In contrast energy-dispersive detectors provide the spectrum of all detectable elements in a single measurement.

X-ray filters are usually placed between the sample and the detector to reduce both the intensity of low energy X-rays from major elements in the sample and the intense secondary electron bremsstrahlung at low X-ray energies. A wide variety of filters has been used, including plastics of different thicknesses, metal foils and

filters containing one or more holes. The choice of absorber material and thickness depends on the sample matrix and the elements of interest [44].

In order to opimize the measurements of Mn, Fe, As, Rb, Sr, Zr and Ba in lead glass using the PIXE method a 150 μm Al filter, a 150 μm Al filter with a 0.1 mm diameter pinhole, Kapton (with thickness 250 μm) and Zn foil (with thickness 50 μm and 100 μm) filters have been studied. In lead-rich material the intense Pb L X-ray peaks particularly obscure the analysis of arsenic and strontium. The intense lead peaks also add to the general background throughout the X-ray spectrum. A pure lead sample was measured using different filters to obtain the relative intensities of lead peaks. By subtracting the overlapping lead peaks and the intense background induced by lead peaks it was possible to evaluate the intensities of arsenic, strontium, rubidium and zirconium peaks.

5.4. The SEM method

5.4.1. General aspects

When the electron beam impinges on a specimen surface, secondary electrons, backscattered electrons, Auger electrons and photons of various energies are produced in addition to characteristic X-rays. In scanning electron microscopy (SEM), the signals of greatest interest are secondary and backscattered electrons, since these vary according to differences in surface topography as the electron beam sweeps across the specimen. In the electron probe microanalyser (EPMA), frequently referred to as the electron microprobe, the primary radiation of interest is the characteristic X-rays. Historically, scanning electron microscope and the electron microprobe evolved as separate instruments even though these two instruments are quite similar, and differ mainly in the ways in which they are used. After the addition of an energy-dispersive X-ray detector in 1968 to an electron probe analyser the coupling of this equipment with the SEM followed. Today most SEMs are equipped with X-ray analytical capabilities [46, 47]. In this thesis (Papers III-VI) the SEM with an energy-dispersive spectrometer (EDS) was

used to determine major, minor and trace elements in old glass fragments. The SEM with a wavelength-dispersive spectrometer (WDS) was used in Paper V.

5.4.2. Electron detectors

The basic form of the SEM image is derived from secondary electrons ejected from the sample by the electrons in the incident beam. Usually these are detected by means of a ‘scintillator ‘ consisting of either plastic or crystalline material which produces light when bombarded with electrons. The light is converted to an electrical signal by a photomultiplier. Secondary electrons are emitted with energies of only a few electronvolts and must be accelerated to several kiloelectronvolts to produce a reasonable output from the scintillator.

The detector arrangement most commonly used in SEMs is the Everhart-Thornley (E-T) type. This has mesh in front of the scintillator, which can be biased to control the collection of electrons. With a positive bias (e.g. +200 V), secondary electrons are attracted on grid and accelerated onto the scintillator by +10kV. If a negative bias is applied to the mesh, secondary electrons are repelled and only backscattered electrons (BSE) are detected due to their high energy. Backscattered electrons can also be detected by solid-state-devices [45-46].

5.4.3. Energy-dispersive spectrometers

In energy dispersive (ED) detectors, the medium used in X-ray detection is silicon or germanium with an electronic band structure in which the valence band is normally fully occupied by electrons and a largely unoccupied conduction band at a higher energy. The two are separated by an energy gap. In a semiconductor detector, some of the energy of the incident radiation is applied to raising electrons from valence to the conduction band, where they are free to move through the lattice. The holes left in the valence band behave like free positive charges. A bias voltage is applied across the detector so that charge carriers (electrons and

holes) move opposite electrodes, producing a signal which enables the X-rays to be detected.

Even the most highly refined silicon contains impurities which have undesirable effects. These are counteracted by introducing lithium using a process known as drifting, hence the name 'lithium-drifted silicon' or 'Si(Li)', detector. Germanium detectors are made of very pure material which does not require the addition of Li. The detector is cooled with liquid nitrogen to minimize electronic noise. Germanium detectors are most suitable for high-energy X-rays. [46, 47].

5.4.4. Wavelength-dispersive spectrometer

X-ray spectrometers of the wavelength-dispersive (WD) type make use of crystal diffraction for wavelength selection. X-rays of wavelength λ are strongly reflected by a crystal of interplanar spacing d when the following condition (Bragg´s law) is satisfied:

$$n\lambda = 2d\sin\theta \qquad (3)$$

where θ is the glancing angle of incidence and reflection and n is the order of reflection, or the number of wavelengths that corresponds to the path difference between rays scattered from successive layers. The most intense reflections normally used in WD analysis are those of the first order (n=1). Higher orders add unwanted peaks to the spectrum. Their intensity is relatively low and they can be suppressed by pulse height analysis.

In the wavelength-dispersive (WD) spectrometer Bragg reflection is used to select a single wavelength at a time. Different wavelengths are obtained by varying the angle of incident and reflection simultaneously. The reflected ray is defined by a slit in front of the detector. Several crystals are needed to cover the full range of relevant wavelengths [44]. The WDS-analyses of this thesis (Paper V) were made using TAP (thallium acid phthallate) crystal (for analyses of Na, Mg, Al, Si), PET (pentaerythritol) crystal (for analyses of P, S, Cl, K, Ca, Ti, Sr, Ba, Zr) and LiF (lithium fluoride) crystal (for analyses of Mn, Fe, Zn, Cu, Pb).

In a WDS, X-rays are detected by means of a proportional counter that consists of a gas-filled tube with a coaxial anode wire and a window through

which X-rays can enter. Incoming X-rays ionize gas atoms, producing free electrons which move to the anode while positive ions move out to the cathode. Each X-ray photon that is absorbed thus produces an electronic pulse. Its size reflects the number of ions produced, which is in turn proportional to photon energy. Pulses are counted to measure X-ray intensities, which are expressed in counts per second.

A commonly used counter gas is argon, with 10 % methane added to improve its properties. However, this is not dense enough to absorb short wavelength X-rays effectively and xenon is sometimes used instead for this purpose. Alternatively, the required absorption can be obtained by using a container filled with argon at higher pressure [46, 47].

5.4.5. Quantitative analysis and ZAF corrections

In quantitative electron induced X-ray analysis, the so-called ZAF corrections are equivalent to the integral in equation (1). The acronym ZAF describes a procedure in which corrections for atomic number effects (Z), absorption (A) and fluorescence (F) are calculated separately from suitable physical models and experimental data. The atomic number correction encompasses both the stopping power and backscattering factors [43, 47].

5.5. Standards

The basis of quantitative electron and proton induced X-ray analysis is the comparison of the intensities of X-ray lines emitted by the specimen with those from reference standards. Usually a separate standard is required for each element even though the composition of the standard should be close to the analysed material. In SEM-EDS measurements absolute concentrations were calculated using the MAC (Micro-Analysis Consultants Ltd., St. Ives, UK) standard no. 3056, the NIST (National Institute of Standards and Technology, USA) glass

standard SRM 620 and the Corning glass standards C and D [48, 49]. Absolute concentrations in SEM-WDS measurements were obtained using the same MAC standard as in the SEM-EDS measurements. In PIXE measurements absolute concentrations were calculated using the NIST (previously NBS) glass standards SRM 620, SRM 89, SRM 611 and the Corning glass standards C and D. The NIST glass standard SRM is soda-lime flat glass. The NIST glass standard SRM 611 contains 61 trace elements at nominal concentrations of 500 ppm by weight in a soda-lime-silica glass matrix. The NIST glass standard SRM 89 is a lead-barium glass powder. For PIXE measurements the powder was packed in a plastic tube covered by Kapton foil.

The absolute concentrations of calcium, manganese, iron, zinc, bromine and strontium in oyster shells have been obtained using the IAEA animal bone standard (Paper VI).

5.6. Measurements

In the PIXE analysis the samples and standards were bombarded with a 2 nA external proton beam from the 2.5.MV Van de Graaff accelerator of Helsinki University. The energy of the protons on the target was approximately 2.4 MeV. The measuring time for lead free glass samples was about 3 min (Papers I, III - V), for lead glass samples about 8 min (Paper IV) and for oyster shell samples about 7 min (Papers II, VI).

In the SEM analysis the glass samples were bombarded with 15 kV electrons from a Jeol JSM 6400 scanning electron microscope at the Institute of Electron Optics of Oulu University. The electron beam current was 1.2 nA and the measuring time was 50 seconds (Paper IV). The other scanning electron microscope used in this work was a Zeiss 962 Digital Scanning Microscope at the Electron Microscopy Unit of the Institute of Biotechnology of Helsinki University. Samples were bombarded with 20 keV electrons and the measuring time was 100 seconds (Paper III).

The WDS analyses of glass samples were made at the Institute of Electron Optics of Oulu University, using a JEOL superprobe 733 scanning electron microscope with an automatic Link Lemas detector system using TAP crystal (Na, Mg, Al, Si), PET crystal (P, S, Cl, K, Ca, Ti, Sr, Ba, Zr) and LiF crystal (Mn, Fe,

Zn, Cu, Pb). All analyses were made using a 15 kV accelerating voltage and a beam current of 15 nA. All measurements were carried out using a measuring time of 40 s for the elements (20 s at peak position and 20 s at background). (Paper V)

5.7. Detection limits

There are many procedures for calculating the detection limits in X-ray spectroscopy. The factors that determine the detection limits in electron and proton X-ray analysis are the counting time, the accelerating voltage, the beam current, the line used to measure the element and the composition of both the sample and the standards. Quite often the detection limits in SEM measurements are determined as three standard deviations of the background [49], while in the PIXE measurements the detection limits are calculated by assuming that the minimum intensity of the peak is three times the square root of the background at full width at half maximum intensity of peak. In this work, detection limits have been evaluated under the latter conditions. For the WDS measurements, this means that whole peak areas of some elements have been measured. Then the peak and background areas at full width of half maximum intensity of the peak were graphically integrated from the whole peak area measurements.

The detection limits of the PIXE method at trace element level are significantly better than the detection limits of the WDS and EDS methods. According to Reed [37], the theoretical detection limits in SEM-EDS measurements are about 0.08 wt%. Typical detection limits for WDS detectors are 0.01wt% [47]. The detection limits with the macro PIXE system for thick targets are of the order 1-10 ppm by weight. The detection limits in the EDS, WDS and PIXE measurements of this work are expressed as ppm by weight, using the MAC standard 3056 in the EDS and WDS measurements and the NIST glass standard SRM 611 and Corning glass standard D in the PIXE measurements. Values are presented in Table 1.

Table 1. The detection limits in the present EDS, WDS and PIXE measurements of a glass matrix with a low Pb-content, expressed as ppm by weight.

Element	EDS	WDS	PIXE
Na	800	160	
Mg	660	20	
Al	530	20	
Si	800	15	
P	790	120	
Cl	1000	30	
K	1000	15	
Ca	930	15	
Ti		20	15
Mn		35	7
Fe		30	5
Co			4
Ni			4
Cu		50	3
Zn		60	3
Pb			2
Rb			2
Sr			2
Zr		100	3
Ba		60	160

The real measuring time using the PIXE method is about 3 min for each sample and each element. In this work the measuring time for each element in the WDS analysis was 40 s. Using the WDS method, the whole peak area measurement takes about 30 min when the step is 0.010 mm and the measuring time/step is 0.2 s. Then the WDS measurement of the peak area at full width and half maximum intensity takes about 3 min, which is similar to the PIXE measuring time but notably longer than the real measuring time of 40 s. Thus the detection limits calculated under the present conditions are minimum detection limits for the WDS method; using the measuring time of 40 s the detection limits are higher while the detection limits for the PIXE measurements are experimental and according to the measurements. In the WDS measurements of old glass, longer measuring times than those used in this work are possible in multielemental analysis. However, higher beam currents damage the sample.

5.8. Homogeneity

The PIXE and SEM methods are surface sensitive. According to M. Mosbah et al. [50], the range of 2.5MeV protons in glass is around 60 μm and the maximum depth of analysis is 30-35 μm. In the usual conditions of SEM analysis, the thickness of the analysed layer is only a few microns [49]. Because the results of this work (Paper V) are being judged against results of "bulk" analyses of homogenized powders, large samples have also been used in the SEM-WDS analyses. In addition, we have chosen analysis points at 5 widely spaced locations on the glass samples instead of taking 5 replicate analyses at a single point. The basis for testing homogeneity is that for a homogeneous sample, the measured standard deviations should fall within the $N \pm 3N^{1/2}$ limits, where N stands for the mean peak counts [46]. Comparing the measured standard deviations in the WDS and the PIXE measurements with the theoretical standard deviations calculated from count statistics, it is apparent that according to the WDS measurements at level of 0.5 wt% (in the Corning reference standard D) Ti, Mn, Fe and Ba are homogeneously distributed while Zn, Cu and Sr are inhomogeneously distributed. On the basis of the PIXE measurements Mn and Fe are inhomogeneously distributed, while Ti, Cu, Zn, Rb, Sr, Zr, and Ba are homogeneously distributed. In the NIST reference glass SRM 611 (at level of 0.05wt%) the trace elements, with the exception of Ti, are inhomogeneously distributed according to the WDS measurements and homogeneously distributed on the basis of the PIXE measurements. The differences between the WDS and PIXE results can be explained by the diameter of beam (0.8 cm in the PIXE measurements and 30 μm in the WDS measurements) but micro inhomogeneity in glass also exists.

5.9. Results of oyster samples

The absolute concentrations of calcium, manganese, iron, zinc, bromine and strontium in the nacreous and prismatic layers of the European oyster *Ostrea edulis* and the average concentrations of these elements as measured in both layers are given in Table 2.

Table 2. Major and trace element concentrations in the prismatic and nacreous layers of shells of the European oyster *Ostrea edulis* and the average values of these concentrations as measured in both layers (in ppm by weight).

Age	Layer	Ca	Mn	Fe	Zn	Br	Sr
4170	Prismatic	417 000	27	88	15	3	640
±100	Nacreous	387 000	16	110	11	9	750
Averages		402 000	22	100	13	6	700
		±15 000	±6	±13	±2	±3	±50

If shells have been used as source of lime in the glass production process, impurities originating from this material are manganese, iron, zinc, bromide, strontium and some other elements, depending of the species of shell used as raw material. Manganese and iron are included in other major constituents of glass, sand and alkali [12]. It is unlikely that we could conclude what part of each impurity originates from each raw material. In addition, the concentrations of these impurity elements which originate from shells should be only some ppms, at most ten even if the whole amount of lime (at the most 20 wt% of raw materials) has been added as shells. If 1/10 of the lime has been introduced into the glass making mixture as shells, then the concentrations of iron and strontium could be detectable. These estimates are given in Table 3. Calculations are based on the average values of these elements measured in the prismatic and nacreous layers, which given in Table 2.

Table 3. The estimated levels of manganese, iron, zinc, bromine and strontium if 20 wt% or 2 wt% of raw materials have been introduced into the glass making mixture as oyster shells (in ppm by weight).

Shells (wt%)	Mn	Fe	Zn	Br	Sr
20	4	25	3	1.5	140
2	0.4	2.5	0.3	0.2	14

6 Comparison of PIXE and SEM with other methods

The PIXE and SEM methods have been widely used in elemental analysis of objects of arts and archaeological finds. The primary purpose of SEM is to produce high resolution images of the surface. The second most common use of the SEM is for determining composition. Brothwell [51] was one of the first to advocate the use of SEM in the analysis of archaeological samples. The use of an external beam in the PIXE analyses is a great advantage; the ability to handle large objects with irregular shapes is of prime importance. Additionally, the lack of charge build-up problems for non-conducting samples eliminates the necessity of coating the material. The disadvantage is that the technique is very surface oriented. Conceptually closest to PIXE and SEM method is X-ray fluorescence (XRF) analysis, where the characteristic X-rays are produced by electromagnetic radiation. For the production of photons, X-ray tubes have traditionally been used. Due to their convenience of use and low cost, radioactive sources are also widely used. The intensity of the radiation emitted by the source is, however, normally lower than that of the tubes; hence, the detection limits are higher than for the tube excitation. The development of synchrotron radiation facilities has also created new prospects for XRF analysis. The detection limits of XRF are normally on the ppm level and are similar to those of PIXE analysis [52-54]. When analysing objects with only very thin corrosion layers, the relatively large analysis depth of XRF for heavier elements as compared to PIXE gives it an advantage in bulk analysis. When the object cannot be moved and one has to go out into the field with equipment, the portable XRF apparatus, based on excitation with radioactive sources, is very useful. The requirement on sample size is not an important restriction in most applications related to art and archaeology, but XRF analysis is preferable when carried out on samples of tens of mg and larger. High sensitivity for heavier elements and very slight sample damage are also advantages of XRF analysis. It is worth noting that although PIXE analysis in a vacuum may partly damage a precious sample, there are examples of very delicate samples which have been successfully analysed in a vacuum, e.g. valuable stamps [54]. Malmqvist has compared PIXE and XRF for application in art and archaeology [55]. In particular, the total reflection X-ray

fluorescence analysis (TXRF) is a powerful analytical tool for trace element determination in various kinds of samples [56]. There are, however many problems connected with this method of glass research. One of the biggest is that the sample should be very thin.

Atomic absorption spectroscopy (AAS) analysis is quite often used for determining elemental composition. This method is capable of high accuracy and sensitivity for a large number of elements found in ancient glasses, but only one element can be detected at a time. The sample must be in a solution, the sample size is 100-500 mg and a single solution cannot always be used for all determinations. The detection limits in AAS are worse than in PIXE. Hughes et al. [57] describe in detail the special problems encountered in the application of atomic absorption techniques in archaeology.

Neutron activation analysis (NAA) is suitable for minor and trace element analysis. The specimen is bombarded with slow neutrons which interact with atomic nuclei of the constituent elements and transform them into unstable radioactive isotopes. These decay by emitting gamma rays with sharply defined energies which are characteristic to the particular element excited. Olin et al. [4] proved that valid information on composition could be obtained, when the sample size is about 20 mg. The detection limits are comparable to those detected by the PIXE method.

In inductively coupled plasma spectroscopy the amount of sample glass could vary from less than hundred milligrams to a few grams. The sample must be in a solution and the determination of three to six elements at a time is possible. Detection limits are worse than in PIXE [7].

In corrosion studies of medieval window glass Dawson et al. [58] have used Auger electron spectroscopy. In structural studies X-ray diffraction has been used with the SEM method. Although glass itself is not crystalline the method has been used for studies of ancient glasses as a way of identifying colouring agents and opacifiers. In glass research a combination of techniques is usually chosen.

7 Conclusions

In the provenance studies of old glass, a good result is obtained on the basis of analysis of about ten elements (Papers I and III); therefore the SEM and PIXE techniques, as powerful multielemental analysis methods, are suitable for resolving problems connected with the origin of an old glass artifact. The SEM-WDS and SEM-EDS methods are suitable for analysing major and minor components of glass samples. Trace element (< 0.1 wt%) analysis is possible using the WDS or PIXE method. By the PIXE method concentrations from 100 wt% to trace element level may be detected. The sample preparation for PIXE analysis of glass artifacts is quite straightforward; after the removal of corrosion layers direct irradiation is often possible. The sample preparation for SEM is time consuming but the sample is not destroyed and is available for further investigations.

The PIXE method is the most sensitive. The detection limits of SEM-EDS, SEM-WDS and PIXE are about 0.1, 0.01 and 0.001 wt%. Concentrations of some trace elements important in glass research such as Ti, Mn and Fe are often in the range 0.1-1.0 wt%; then analysis using any of these three techniques is possible and the knowledge about the accuracy and precision of the analysis method can help one choose the most appropriate technique. The accuracies of WDS measurement of Ti, Mn, Fe, Zn, Cu and Ba with concentrations at 0.5 wt% are comparable to values obtained for PIXE, but precisions are 20-40 % when in the PIXE measurements they are under 10 %, with the exception of Ti. At the level of 0.05 wt% the precisions are about 10 % and accuracies 20 % in the PIXE measurements, while in the WDS measurements they are 20-50 % and 40-80 % with the exception of the accuracies for Ti and Mn which are 1 % and 11 % and thus more comparable to the approximately 20 % values of the PIXE measurements (Paper V).

The EDS method is comparable to the WDS method in the lead glass analyses as well. The greatest difference is in the measurement of Na when the concentration of Na is about 1 wt%. The accuracy and the precision of Na in the WDS measurements are about 1 %, but in the EDS measurements they are nearly 10 % and 30 % (Papers IV-V).

The SEM and PIXE methods are surface sensitive. On the macro scale (in the PIXE measurements when the diameter of the proton beam was about 0.8 cm) the glass is quite homogeneous when the measured and theoretical standard deviations of trace element concentrations as determined using this method are compared. On the micro scale (in the WDS measurements when the diameter of the electron beam was 30 μm) the glass is homogeneous when the concentrations of trace elements are at a level of 0.5 wt% but inhomogeneous when the concentrations are at a level 0.05 wt%. Thus the analysis results of the SEM and PIXE methods are quite comparable with results of bulk analyses of homogenized powders (Paper V).

The detection limits of the EDS, the WDS and the PIXE measurements are calculated assuming that the minimum detectable peak is three times the square root of the background at full width at half maximum intensity of the peak. The detection limits in the EDS measurements are 530-1000 ppm by weight, in the WDS measurements 15-160 ppm by weight and in the PIXE measurements 2-15 ppm by weight. In the lead glass samples using the PIXE method the 50 μm thick zinc filter improves the S/B (peak/background) ratio and the detection limits of Ba at the concentration levels of 10.8 and 1.25 wt%. The best detection limits in lead glass for Mn and Fe can be obtained by a 250 μm thick Kapton filter and for As, Rb, Sr and Zr by a 150 μm thick aluminum filter with a 0.1 mm diameter pinhole (Paper V).

Investigations on deposition of minor and trace elements in sea shells may yield useful information for pollution studies (Paper II) and for ”fingerprint” studies of ancient glasses (Paper VI). The PIXE technique is a fast , convenient method for determination of different elements in shell samples because it requires minimal sample preparation and allows simultaneous determination of a number of elements. According to the measurements the Zn/Ca and Sr/Ca ratios seem to be very consistent throughout the whole 4200 year period. However, the Mn/Ca and Fe/Ca ratios are higher in recent shells and Pb has been detected only in recent shells from the bay in front of Dublin (Paper II). In the glass manufacturing process, the possible impurity elements originating from oyster shells are manganese, iron, zinc, bromine and strontium. If 1/10 of the lime has

been introduced into the glassmaking mixture as shells, then the concentrations of iron and strontium could be detectable. If the whole amount of lime needed in the glass production process has been added as shells, then the concentrations of manganese, iron, zinc and strontium are detectable on the ppm level. The origin of this manganese, iron, zinc and strontium remains unclear because other raw materials of glass, sand and alkali also include these elements as impurities. Bromine found in some samples from the museum Aboa vetus in Turku has most probably been introduced as part of chlorine salts (Na Cl, KCl) used as a source of alkali (Paper VI).

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References

[1] W. Geilmann, *Glastech. Ber.*, 27(1954)456.

[2] J. Leiber, W. Czygan and H. Maus, *Zeitschr. Archäol. Mittelalt.*, 13(1985)77.

[3] G. Rauret, E. Casassas and M. Baucells, *Archaeom.*, 27(1985)195.

[4] J. S. Olin, in *Archaeological Chemistry*, edited by C. W. Beck, Adv. In Chem. 138, American Chemical Society, Washington D. C., 1974.

[5] I. Kuleff, R. Djingova and G. Djingov, *Archaeom.*, 27(1985)185.

[6] J. Frána, A. Mastalka and N. Venclová, *Archaeom.*, 29(1987)69.

[7] P. Mirti, A. Casoli and L. Appolonia, *Archaeom.,* 35(1993)225.

[8] M. J. Baxter, H. E. M. Cool, M. P. Heyworth and C. Jackson, *Archaeom.*, 37 (1995)129.

[9] G. A. Cox and K. J. S. Gilles, *Archaeom.,* 28(1986)57.

[10] Pliny, *Natural history*, libri XXXVI, engl. transl. in ten volumes by D. E. Eichholz, repr., William Heinemann Ltd., London, 1962.

[11] S. Frank, *Glass and Archaeology*, Academic Press, London 1982.

[12] W. E. S. Turner, *J. Soc. Glass Techn.,* 40(1956)39.

[13] P. Vandiver, in *Early pyrotechnology: the evolution of the first fire-using industries,* edited by T. A. Wertime and S. F. Wertime, Smithsonian Institution Press, Washington D. C., 1982.

[14] I. C. Freestone, *Mat. Res. Soc. Symp. Proc.*, 267(1992)739.

[15] J. Henderson, *Archaeom.,* 30(1988)77.

[16] S. Hreglich and M. Veritá, in *Scanning Electron Microscope II*, Scanning Electron Microscopy Inc., Chigaco, 1986.

[17] D. Gihwala, L. Jacobson, M. Peisach and C. A. Pineda, *Nucl. Instr. Meth. Phys. Res.,* B3(1984)408.

[18] M. Peisach, *Nucl. Instr. Meth. Phys. Res.,* B14(1986)99.

[19] S. J. Fleming and C. P. Swann, *Nucl. Instr. Meth. Phys. Res.,* B85(1994)864.

[20] W. H. Zachariasen, *J. Amer. Chem. Soc.,* 54(1932)3841.

[21] R. J. Charleston, *Archaeom.,* 3(1960)1.

[22] S. Strobl, *Glastechnik des Mittelalters,* Gentner Verlag, Stuttgart, 1990.

[23] F. L. Harding, in *Introduction to Glass Science*, edited by L. D. Pye, H. J. Steves and W. C. LaCourse, Plenum Press, New York, 1972.

[24] W. A. Weyl, *Colored Glasses*, The Society of Glass Technology, Sheffield, 1951.

[25] R. G. Newton, *Glass Techn.,* 19(1978)59.

[26] S. Hreglich, B. Profilo and M. Veritá, *Corp. Vitr. Lett.,* 32/34(1980)16.

[27] S. Hreglich and M. Veritá, *Scan. El. Micr.,* 2(1986)485.

[28] J. S. Gillies and A. Cox, *Glastech. Ber.,* 61(1988)75.

[29] R. Raw, *J. Soc. Glass Techn.,* 39(1955)128.

[30] K. Janssens et al., *Nucl. Instr. Meth. Phys. Res.*, B109/110(1996)690.

[31] C. M. Yonge, *Oysters*, Collins, London, 1960.

[32] J. D. Taylor, W. J. Kennedy and A. Hill, *Bull. Br. Mus. Nat. Hist. (Zool.),* Suppl.3(1969)1.

[33] R. C. Brusca and G. J. Brusca, *Invertebrates*, Sinauer Associates, Inc., Sunderland, USA, 1990

[34] D.A. Seagar, J. D. Collins and J. P. Riley, *J. Mar. Biol. Ass.,* 51(1971)131.

[35] J. R. Dodd, *Geochim. Cosmochim. Acta,* 29(1965)385.

[36] P. Koivunen, 1998, private communications.

[37] S. J. B. Reed, *Electron microprobe analysis and scanning microscopy in geology,* Cambridge University Press, Cambridge, 1996.

[38] H. G. J. Mosley, *Philos. Mag.,* 26(1913)1024.

[39] H. G. J. Mosley, *Philos. Mag.*, 27(1914)703.

[40] R. Castaing, PhD thesis, Univeristy of Paris, 1951.

[41] L. S. Birks el al., *J. Appl. Phys.,* 35(1964)2578.

[42] T. B. Johansson, K. R. Akselsson and S. A. E. Johansson, *Nucl. Instr. Meth.* 84(1970)141.

[43] S. A. E. Johansson and J. L. Campbell, *PIXE: A Novel Technique for Elemental Analysis*, John Wiley & Sons, 1988.

[44] D.G. Fraser, in *Microprobe Techniques in the Earth Sciences,* edited by P. J. Potts et al., Chapman & Hall, London 1996.

[45] J. R. Bird, P. Duerden and D. J. Wilson, *Nucl. Sci. Appl.* 1(1983)357.

[46] S. B. J. Reed, in *Microprobe Techniques in the Earth Sciences,* edited by P. J. Potts et al., Chapman & Hall, London 1996.

[47] J. I. Golstein et al., *Scanning Electron Microscopy and X-ray Microanalysis: A Text for Biologists, Material Scientists, and Geologists,* 2nd ed., Plenum Press, New York 1992.

[48] R. H. Brill, in *Proceedings of the ninth international congress on glass,* Versailles, 1971, vol.3, edited by International Commission of Glass, Institut du Verre, Paris 1972.

[49] M. Veritá et al. *Archaeom.*, 36(1994)231.

[50] M. Mosbah et al., *Nucl. Instr. Meth. Phys. Res.,* **B 104,** 481 (1995).

[51] D. Brothwell, in *Science in Archaeology*, edited by D. Brothwell and E. Higgs, 2nd ed., Thames and Hudson, London 1969.

[52] M. Hall and L. Yablonsky, *Archaeom.*, 39(1997)369.

[53] M. S. Shackley, *Am. Antiquity,* 60(1995)531.

[54] E. M: Johansson et al., *Nucl. Instr. Meth. Phys. Res.,* B14(1986)45.

[55] K. G. Malmqvist, *Nucl. Instr. Meth. Phys. Res.,* B14(1986)86.

[56] P. Wobrauschek and C. Streli, *AIP Conf. Proc.,* 389(1997)233.

[57] M. J. Hughes, M. R. Cowell and P. T. Craddock, *Archaeom.,* 18(1976)169.

[58] P. T. Dawson, O. S. Heavens and A. M. Pollard, *J. Phys. C: Solis State,* 11(1978)2183.